

AN INVESTIGATION INTO STEP POLYMERIZATION VIA LOW VALENT  
TITANIUM COUPLING OF ISOCYANATE COMPOUNDS

By

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Dedicated to my mother Sarah who taught me no taught  
no matter how tough it seems to get

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**AN INVESTIGATION INTO STEP POLYMERIZATION VIA LOW VALENT  
TITANIUM COUPLING OF DICARBONYL COMPOUNDS**

By

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May 1989

Chairman: Dr. Kenneth R. Wehner  
Major Department: Chemistry

In any step polymerization the propagation chemistry must be clean and essentially complete for high polymer to form. Only a dozen or so reactions satisfy the demands of step polymerization. With this challenge in mind, the viability of carbonyl coupling as the process of low valent titanium has been investigated as a new condensation type step polymerization mechanism to cross poly(vinylene) and polyacetal polymers.

The reaction chemistry of Mukoyama and McMurry was altered as a series of model compound studies in order to improve reaction yields such that the chemistry would be suitable for step polymerization. Near quantitative yields were achieved for 2 furfural and 2 thiophenecarbaldehyde suggesting that carbonyl coupling would be a candidate polymerization reaction.

Single crystal X ray structural analysis of the heterocyclic vinylene model compounds prepared by this chemistry unequivocally showed that these structures are essentially flat relative to steric bulk. Further these structure proofs showed that only one conformation exists in which such heterocycles were oriented for steric bulk that steric interaction is minimized. This research suggests that very flat, highly regular heterocyclic polymers could exist, in which steric bulk between polymer chains would be reduced.

Characterization of the putative model compounds with a third shift reagent has more completely elucidated the mechanism of  $\text{TiCl}_4$ -induced coupling. A preliminary formation of the  $\beta$ -il dimer over the  $\alpha$ -il dimer supports the speculation that the anionic mechanism proceeds through a cyclic intermediate involving a low valent titanium center. An  $^{18}\text{O}$  labeling study via mass spectrometry unequivocally defined the mechanism of hydrolysis in this chemistry.

Examining these model compound results in the polymerization of thioetheryl compounds showed that while oligomers and low molecular weight polymers can be formed, polymers with molecular weights exceeding 5000 could not be synthesized. Solubility and mechanistic explanations for these results are presented.

A three fold increase in molecular weight was observed when synthesizing the most flexible polyimide ester that the polyoxaphosazene. corroborating previous evidence regarding the influence of chain flexibility. Rigid polymer structures are less soluble, and a concept to produce soluble, yet potentially rigid, polymer structures is presented, which is based on the incorporation of bulky, thermally labile substituents on the chain itself.

## CHAPTER 1 INTRODUCTION

Successful polymer chemistry is based on reactions which are completely productive and which join one molecule to another. The assembly process can be divided into two categories, chain propagation and step propagation. This research has focused on a study of indirect coupling chemistry via low valent transition metals to produce polymers by step propagation reactions.

All step polymerizations fall into one of two categories depending on the type of monomers employed [1]. The first involves two different bifunctional or polyfunctional monomers possessing one type of functional group each, while the other involves a single monomer containing both types of functional groups. These two groups of reactions can be represented in a general manner by Equations 1-1 and 1-2, where A and B represent the two different types of functional groups.



The characteristics of these two types of step polymerizations are similar. The universal synthesis of high molecular weight polymer using any step polymerization reaction is generally more difficult than the corresponding small molecule reaction, since high polymer can only be achieved at unusually complex conversions. Carothers [2] illustrated the importance of high conversion in step polymerization with the derivation of an equation which relates the degree of polymerization  $\bar{X}_n$  to the extent of reaction  $p$ , assuming a perfect balance of stoichiometry:

$$\overline{X}_n = (1 - p)^{-1} \quad \text{Equation 1-3}$$

$\overline{X}_n$  is defined as the total number of monomer molecules initially present divided by the total number of molecules in a given sample or mass sample.  $p$  is the average number of functional units per polymer chain. The extent of reaction  $p$ , which has a value between 0 and 1, is the fraction of functional groups which have reacted.

In the synthesis of a small organic molecule, a 90% conversion of functional groups to product is considered a good yield. However, if the same degree of conversion occurs during a step polymerization, the degree of polymerization equals only 10 units based on Carothers' equation. Even if the extent of reaction improves to 95%, the number of repeat units only doubles. Based on this numerical relationship, high molecular weight polymer will not form until the extent of reaction reaches greater than 99%.

That need for very high conversion places current stringent requirements on any reaction to be used for step polymerization. It must be a clean reaction with a favorable equilibrium and must be free of any side reactions which might inhibit propagation. These stringent requirements are met by a relatively small fraction of the reactions used to synthesize small molecules, and therefore, any research involving the development of a new coupling reaction or even the evaluation of a present system as a possible method for step polymerization, is always regarded with great interest.

### **Reactive Coupling of Carboxylic**

#### **General Methods Used Before the 1970s**

Reactive coupling of carboxylic is one step reaction which has not been investigated as a possible route for synthesizing polymers. Prior to the 1970s phenylisocyanate [3], diisocyanate technique [4] and reduction by metal in appropriate solvents [5] were the most methods used to accomplish reductive coupling, all of which

result in primary formation of pinacols. In the case of photoinduction, many ketones, such as benzophenone, can be coupled photochemically yielding the pinacol in a greater than 50% yield (Figure 1-1). The reaction is a slow process, however, with the possibility of side reactions occurring and thus is not a reaction for forming polymers.

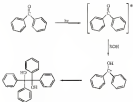


Figure 1-1: Photoinduced coupling of benzophenone

In the 1960s a large amount of research was directed to the electrolytic reduction of aldehydes and ketones to their respective pinacols [6]. The most extensive studies of the macrocyclic reduction of benzophenone for instance, have been those of Brown and coworkers [9] who obtained the pinacol in a 33% yield, which again is too low for polymer chemistry (Figure 1-2). In addition, bis-allylbenzyl ether was also produced as well as appreciable amounts of non-dissoluble compounds.

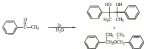


Figure 1-2. Electrolytic Reduction of acetophenone

Reductive coupling of carbonyls can also be accomplished by electron donation from a metal such as magnesium ( $Mg$ ), where the metal is generally activated with a mercury salt to form an amalgam, which can then be reacted with a ketone to produce the pinacol hydride in a 50 to 80% yield (Figure 1-3).



Figure 1-3. Reductive coupling of ketones by amalgamated magnesium.

While all three of these reactions are viable methods for reductively coupling carbonyls, their yields are low and the possibility of unwanted side reactions has given to consider them suitable for ring polymerization.

#### Coupling of Carbonyls with Low-Valent Tungsten and Thorium

In 1973 Shapiro *et al.* [7] reported the unprecedented use of low-valent tungsten to couple aldehydes and ketones to diols. The active coupling reagent is generated by addition of butyllithium to tungsten hexachloride in THF (Figure 1-4) and although a wide range of aldehydes and ketones were coupled, yields for the resulting diols were all average low. The highest yield of 76% was obtained in the coupling of benzaldehyde.



Figure 1-4. Reductive coupling of a carbonyl by low-valent organotin.

During that same year, Mukaiyama et al. [8] reported that a low-valent organotin compound, generated from  $SnCl_4$  and  $Zn$ , reduced aldehydes and ketones to the corresponding pinacols as well as alkenes depending on reaction conditions (Figure 1-5). Tylicki and Woloszewski [9] of Polkad reported similar results with a  $SnCl_4$ /Mg combination.

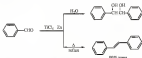


Figure 1-5. Reductive coupling of benzaldehyde using Mukaiyama's reagent.

In a typical experiment, a suspension of zinc powder in THF was slowly added to a mixture of benzaldehyde and  $SnCl_4$  in THF at  $-10^\circ C$  under argon. The yellow solution immediately changed to purple and then turned dark brown. After the reaction mixture was stirred for 3 hours at  $0^\circ C$ , followed by alkaline hydrolysis with 10% potassium carbonate solution and decoloration treatment, 1,2-diphenyl-ethane-1,2-diol and stilbene were isolated as 86% and <1% yields, respectively. In the absence of water, the dehydrogenation reaction to stilbene took place by refluxing the reaction mixture in toluene for 4 hours. The more stable cis-stilbene was obtained as a 54% yield.

The significance of the work of Mikoyan et al., other than as a direct analogy for the synthesis of pinacols and -diols, is that near-quantitative yields are obtained in the synthesis of these compounds. High yields, however, are observed only in the coupling of aromatic aldehydes and ketones (Table 1-1). This data suggests, therefore, the possibility of using indirect coupling of carbonyls as a mode for ring polymerization, at least in the case of aromatic aldehydes and ketones.

Table 1-1 Reaction of carbonyl compounds with  $\text{TiCl}_4$  and  $\text{Et}_3\text{Al}$

Solvent	Temp	Compound	Pinacol	Glycol
THF	25°C	benzaldehyde	80%	1%
THF	reflux	benzaldehyde	0%	90%
THF	25°C	benzaldehyde	80%	1%
dioxane	reflux	benzaldehyde	0%	90%
dioxane	85°C	3-phenylpropanal	75%	8%
THF	reflux	3-phenylpropanal	80%	7%

### Search for Low-Valent Titanium Chemistry in Mikoyan and Other Investigations

Before any attempt can be made at polymerization chemistry, it is imperative to understand the chemistry involved. For example, what are the optimum conditions necessary for high yields, and are there any other systems which give similar results? Although Mikoyan and Tyrlak were the first to report the use of low-valent titanium for the purpose of coupling carbonyls to diols and pinacols (2,3), McMurry and co-workers have performed the most extensive research into the range of this chemistry as well as the pinacol-making phase (12-17). For this reason, many consider coupling by low-valent titanium to be Mikoyan chemistry (18).

The research of McMurry et al. did not involve the  $\text{TiCl}_3/\text{Zn}$  system of Makosyan et al. but dealt mainly with a  $\text{TiCl}_3/\text{LiAlH}_4$  combination [10,11], which gave better results with aliphatic systems. Table 1-2 shows reactions carried out by McMurry et al., with yields ranging from 80 to 90%. McMurry noted that the coupling of saturated aliphatic ketones to alcohols was easier [12] whereas successful results seemed to be dependent on specific features of organic acid. As a result, they investigated  $\text{TiCl}_3/\text{K}$  [13],  $\text{TiCl}_3/\text{Li}$  [13] and  $\text{TiCl}_3/(\text{Zn}-\text{Cu})$  [14] reducing systems and found the results to be far more reproducible, yet, experimentally McMurry and co-workers preferred the  $\text{TiCl}_3/(\text{Zn}-\text{Cu})$  system since working with potassium and lithium are potentially more dangerous [15].

Although the research of McMurry et al. only concerned the formation of alcohols, Corey and co-workers [16] investigated several different types of reducing systems for pinacol boronates and found that a  $\text{TiCl}_3/\text{Mg}(\text{Clg})$  system gave the best overall yields for their applications (Table 1-3).

#### Nature of the low-valent titanium reagent

Understanding the exact nature of the low-valent titanium reagent before, during and after coupling of the carbonyls is important in the application of McMurry Chemistry to polymerisation. This aspect of the chemistry, however, has generated the greatest number of questions and debate. Equations 1-4 and 2-5 show the general two-step reduction process, where [B] is the activated monomer-reagent and [B-Cl] is the by-product after dimerization or hydrolytic work-up.



Table S.2 Reactions performed by McPherson et al. with  $\text{TaCl}_5$  and  $\text{LiAlH}_4$ 

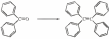
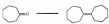
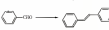

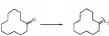
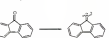







	Yield
 <chem>O=C(c1ccccc1)c2ccccc2 &gt;&gt; C(c1ccccc1)Cc2ccccc2</chem>	95
 <chem>O=C1CCCCC1 &gt;&gt; C1CCCC1C2CCCC2</chem>	85
 <chem>O=Cc1ccccc1 &gt;&gt; C(c1ccccc1)Cc2ccccc2</chem>	45
 <chem>O=C1C2CCC1C2 &gt;&gt; CC(=C)C1C2CCC1C2</chem>	88
 <chem>O=C1C2CCC1C2C3=CC=CC=C3 &gt;&gt; CC1=CC=CC=C1C2CCC1C2C3=CC=CC=C3</chem>	60
 <chem>O=C1C2CCC1C2C3=CC=CC=C3 &gt;&gt; CC1=CC=CC=C1C2CCC1C2C3=CC=CC=C3</chem>	90

Table 1.1 Reactions performed by Corey et al. with  $\text{TiCl}_4\text{-In}(\text{Hg})$ 

		Yield
	$\longrightarrow$	 84
	$\longrightarrow$	 80
	$\longrightarrow$	 60
	$\longrightarrow$	 50

The nature of the active coupling species  $[\text{M}]$  (in particular the formal valence state of titanium in  $[\text{M}]$  and/or the resulting  $[\text{M-O}]_2$ ) was initially unknown. Both Makolyma et al. [8] and McMurry et al. [10] initially proposed the formation of  $\text{Ti(II)}$  by electron donation from  $\text{Zn}$  or  $\text{LiAlH}_4$ . McMurry felt this evidence in support of the hypothesis came from observation of the black color characteristic of  $\text{Ti(III)}$  species [7].

In a later paper, however, McMurry and Fleming [12] modified their procedure using Fieser's general method for preparation of activated metals [30]. Fieser and Flinnell developed this protocol in 1972 for generating magnesium metal in a very inert state to be used in the preparation of Grignard reagents. The general protocol for generating finely divided metal involves addition of a magnesium halide by reflux in an inert aprotic solvent with an alkali metal under an inert atmosphere. Refluxing yields a fine black powder of magnesium metal which can be immediately used to prepare the Grignard reagent by simple addition of a alkyl or aryl halide (Figure 1.4). This modification therefore involved the

reflux of  $\text{TiCl}_3$  with the reducing agent in THF prior to the addition of the alkylide or ketone, forming what is considered to be an active  $\text{Ti(II)}$  powder



Figure 1.6. Preparation of activated organotitanium for use in Grignard reactions

A comparison of the yields of olefin production from the various systems shows that active  $[\text{M}]$  is by far the most potently efficient in coupling, regardless of however different the reduction conditions may be. This comparison, as well as the common color change observed for all the reactions, is taken as an indication that various reducing agents produce rather similar  $[\text{M}]$  species [11].

Dunn and co-workers [12] have reported the most extensive investigation into the nature of  $[\text{M}]$  via electron microscopy, thermogravimetry, infrared spectroscopy, and electron spin resonance. Their observations led to the conclusion that  $[\text{M}]$  is a colloidal suspension of titanium particles, mostly in the zero valence state, which is stabilized by weak interaction with the solvent. A model of such a particle is shown in Figure 1.7.

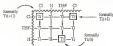


Figure 1.7. Model of an active titanium particle proposed by Dunn et al.

The outer side resembles metallic titanium, while on the surface, titanium can be in a higher valence state, particularly when bonded to chlorine or oxygen atoms. The number and strength of the ligand bonds determine the formal valence state of titanium as a

given position on the surface. Formal bulk selectivity is then an average over all transition states and is dependent on the reducing agent used.

The reactivity of [M] towards the choice of solvents largely is hydrocarbonous and others. Solvents investigated by Dunn et al. included benzene, cyclopentanone, toluene, formic, dimethylformamide, acetonitrile, acrylonitrile, glycerol, diglyme, and diethyl ether. In pyridine, the metal reduction could be performed with all reducing agents (as judged from the appearance of a black suspension) but the strong chelating effect of the nitrogen would not allow coupling. Using diethyl ether as a solvent, they observed the formation of a metallic mirror on the walls of the reaction vessel suggesting completion, but clusters were still formed in good yields. Of all the solvents tested, however, THF performed best in all instances, since [M] could remain as small particles.

Dunn and coworkers also sponsored mechanistic studies for the formation of [M]. Based on the amount of cluster formed as well as extracted starting material, they calculated the optimum conditions to be reached at a  $\text{TiCl}_3/\text{K}$  ratio of 1:3.3 and at a  $\text{TiCl}_3/\text{Et}_3\text{g}$  ratio of 1:1.7. In each case, a three-electron transfer took place, corroborating McMurry's conclusion that [M] contains  $\text{Ti}^0$ .

Since Tyrlik and Meloshewitz [9] suggested that the  $\text{TiCl}_3/\text{ketone}$  ratio could be important, Dunn and coworkers also examined the parameter in the McMurry reaction and found that the most efficient  $\text{TiCl}_3/\text{ketone}$  ratio is at least 1:1. At lower ratios the substantial amount of ketone is left unreacted. Therefore, only one carbonyl molecule can be coupled per titanium atom, making it unlikely that coupling proceeds via a single Ti atom but rather takes place on the surface of a microcrystalline cluster.

As in the case of [M], Dunn and coworkers evaluated [M-O] using various techniques to obtain a plausible model. The nature of [M-O] after desilylation was discussed by McMurry et al. [17] for the most part to be primarily  $\text{TiO}_2$ . Dunn and coworkers report, however, that [M-O] was different from  $\text{TiO}_2$  for several reasons. After coupling, a black color persists, which indicates that  $\text{TiO}_2$  (which is white) is not the final

Ti derivative of the McMurry reaction. Prolonged treatment of the olefin with the olefin-derived species (M-O) can be expected. A fresh portion of  $\text{La-Mg}_2$  reduces (M-O) to the active form (M), which is capable of coupling a fresh batch of olefins in good yields.

Further information about the nature of (M-O) came from ESR spectra obtained after addition of  $\text{TiCl}_3$  to olefins. Signals were very similar to those of (M-O), and must be due to  $\text{Ti(III)}$ , which is a free radical in the olefinic bond. Davis and coworkers<sup>10</sup> interpreted the iron-dependent TI signal as due to (M-O) containing  $\text{Ti(III)}$  as bonded to olefin species (Figure 1-8).



Figure 1-8 Model for (M-O) containing  $\text{Ti(III)}$  as bonded to olefin

### Cyclohexyl mechanism of McMurry reaction

Both Makaryann et al.<sup>16</sup> and McMurry et al.<sup>17</sup> proposed reaction mechanisms for the low-valent titanium coupling process. The major question to answer was whether the reaction proceeds through an oxygen intermediate, with each oxygen coordinated to a separate titanium atom, or whether the reaction proceeds through a cyclic intermediate, with two oxygen-coordinated to one titanium atom forming a bridge (Figure 1-9).

McMurry and coworkers<sup>17</sup> were able to differentiate between these two routes by the reduction of *cis*-8,10-dodecadiol and *trans*-8,10-dodecadiol (Figure 1-10).

Reduction was done by exposure of the diols to  $\text{TiCl}_3/\text{K}$  followed by desorption to the olefins. Reduction of the *cis*-isomer proceeded smoothly to yield the corresponding cyclohexylcyclohexane. Reaction of the *trans* isomer under identical conditions,



Laser-Demo and coworkers [14] were able to describe a more detailed mechanism based on the information they accumulated about the nature of  $[M]$  and  $[M-C]$ . In the first step the carbonyl becomes attached to a free carbon atom on osmium, and the coupling proceeds via a radical mechanism, as started by an osmium transfer from osmium to the carbonyl molecule. Quantitative measurements of radical concentrations were not performed.

The radicals can now react in two ways (Figure 1.11). They either dimerize to osmium peroxide or form alcohols (and hydrocarbons) as a result of being quenched by species of dissolved osmium hydrogen from  $LiAlH_4$  or  $THF$ . Addition of  $THF$  prior to the addition of the carbonyl results in a decrease of alcohol production.

The majority of the radicals will dimerize under proper experimental conditions. Demo specifies that this step is rate determining and not the subsequent cleavage of the C-O bonds. If abstraction of oxygen from the peroxide were the most difficult step, the corresponding peroxide should be formed in higher concentrations.

After the formation of the osmium peroxide the two C-O bonds are broken in consecutive steps, as is suggested by the occurrence of an epoxide as a side product in the coupling of methyl oxides. The work of the mechanism is an osmium bonded to  $[M-C]$ , which is then released by standard work-up procedures.

### Extension of Laser-Demo-Typical Coupling to Dual Polymerization

Since the introduction of low osmium osmium coupling by Mikoyan et al. [4], a great deal of work has been performed in the evaluation and improvement of the procedure. Surprisingly, no one has ever reported yields equivalent to those obtained with the  $TiCl_3$ -Zn system. Extending Mikoyan chemistry to ring polymerization requires the coupling of osmium compounds generating two carbonyl functionalities per molecule. One exposed to the  $TiCl_3$ -Zn complex, the polyosmium peroxide, osmium could either be reduced to form a polyosmium or hydrolyzed to create a polyphoscol (Figure 1.12).

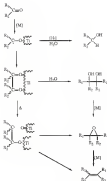


Figure 1-11 Proposed reaction mechanism by Gerni et al

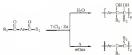


Figure 1-12. Extension of zinc-aided titanium chemistry to ring polymerization

Polypyrrolenes are of interest due to the conjugated nature of their polymer backbones creating the possibility of conductivity [21]. Conductive polymers synthesized by other methods are often low *m*-molecular weight, which has generated interest in the development of improved methods for their synthesis. Polypyrrolenes would be of interest because they are a novel class of polymers, which as of yet have not been made by any other method of polymerization.

Interestingly enough, the coupling of decarbonyl compounds by tributyltin chemistry is not a novel concept. Baumann and coworkers [22] were the first to couple dialdehydes and diketones followed by McMurry [14], but their interest was solely in the intramolecular coupling of the functional groups yielding rings (Figure 1-13).



For *n* = 2 to 30

Figure 1-13. Intramolecular coupling of decarbonyl compounds

To study this chemistry as a polymerization mechanism, it is not sufficient to simply prepare decarbonyl monomers and couple them to polymers. Although

polymerization as the ultimate goal, there are many questions directly concerning the formation and characteristics of such polymers which can only be answered by a thorough model compound study. For instance, are the high yields of Mukaiyama's system reproducible and if so, do these yields extend to other aromatic compounds not yet explored, such as heteroaromatic aldehydes and ketones? What are the expected conformations and configurations within the repeat unit of the polymers and how might they influence polymer properties?

The goal of this research was to evaluate the viability of low-valent osmium chemistry (specifically the Mukaiyama system) as a step polymerization mechanism. Model compound research elucidated the chemistry and its viability for coupling heteroaromatic aldehydes at high yields. Characterization of these model compounds has permitted an evaluation of possible mechanistic routes and has given insight into projected conformations and configurations within the corresponding polymers. Extension of this chemistry to the synthesis of polymers has been limited to basic representative compounds for both aromatic and heteroaromatic aldehydes and ketones.

## CHAPTER 2 EXPERIMENTAL

### General Information

All NMR spectra were obtained with either a Varian JNM 300L 60 MHz NMR Spectrometer or a Varian XL 300 NMR Spectrometer. Chemical shifts are reported in parts per million ( $\delta$ )-downfield from the internal reference tetramethylsilane. All spectra were taken in deuterio-dichloromethane except for polymers which were run in deuterated dimethyl sulfoxide. Infrared spectral analysis was performed on a Perkin Elmer 341 Spectrophotometer with percent transmission being recorded relative to two runs of the sample. Boiling points were obtained from either a Thomas Hoover Capillary-Making Point Apparatus or a Fisher-Johns Making Point Apparatus, and all values are uncorrected. Product purity was determined by a Hewlett Packard 2180A Series Gas Chromatograph, while elemental analyses were performed by Atlantic Microlab, Inc. in Norcross, Georgia. Single crystal structure determinations were performed on a Nicolet RMC X Ray Diffractometer and mass spectroscopic data were obtained from a Finnigan 4000 Gas Chromatographic Mass Spectrometer. Some molecular weight data was obtained from a Waters Vapor Pressure Osmometer.

Unless otherwise specified, reagents were obtained from Aldrich Chemical Company. Solvents were purchased from Fisher Scientific and were distilled A.C.S. reagent grade. Argon used in the coupling reactions was purchased from Liquid Air Inc. in large cylinders.

### Synthesis of $2,2'-(O_2C)_2$ Reductive Complexes for Coupling Reactions

All coupling reactions involved the formation of the *trans*-dicyanide reductive complex before addition of the aldehyde or ketone. This procedure incorporated methods reported

isobutene [8,12], as well as some modifications which increased the maturity and overall efficiency of the reductive complex.

Into a 250 ml, 3-necked, round bottomed flask which had been evacuated, flamed dried and flushed with argon, was placed high purity, 100 mesh zinc powder (1.58 g, 36 mmole). Argon gas was dried by bubbling through concentrated sulfuric acid, followed by a column of sodium hydroxide pellets, and finally a column of anhydrous calcium sulfate (Dowcor). A rubber septum was placed in the center neck, a condenser with drying tube was placed in a side neck, and a slow stream of argon was maintained through the flask. THF (50 ml), which had been dried by reflux with sodium hydride and distilled before each reaction, was syringed through the septum and cooled to  $-60^{\circ}\text{C}$  using a dry ice  $\text{CCl}_4$  bath. The  $\text{TiCl}_4$  (3 ml, 18 mmole) was carefully injected into the THF with stirring, resulting in a clear green-yellow solution.  $\text{TiCl}_4$  was purchased in 250g-quantities in a flask / lead matrix with a purity of 99.9%, and over the years on the Sure-Seal bottle showed signs of decomposition (after four or five years, a new bottle was purchased). The mixture was refluxed over time, causing the color to change to blue then to black. The complex was allowed to cool before addition of the carbonyl compound.

### Model Chelate Formation by Reductive Coupling of Carbonyls

#### Synthesis of the Model Compound Trans-*Silene*

Although trans-silene had been previously synthesized by Ishikawa and coworkers [14], this reaction was repeated for the purpose of verifying their results. Modifications of their procedure, however, was necessary to obtain near quantitative yields.

A solution of benzaldehyde (1.2 ml, 12 mmole) in 10 ml of dry THF was syringed into the reaction flask containing the  $\text{TiCl}_4/\text{Zn}$  reductive complex and refluxed for two hours (while still maintaining an argon atmosphere). After cooling to room temperature, approximately 60 ml of petroleum ether was added causing a vacuum flask precipitate to cling to the walls of the flask. A cloudy white solution remained which was easily poured

was a filter. The black residue, which consists of inorganic salts, tars and unreacted zinc was retained in the reaction vessel, where it was washed with petroleum ether. Although the black residue was still an irritant at this point, no problem was encountered in exposing the black material to the air during the washing procedure. The two fractions were combined, placed in a rotary evaporator and the solvent removed, leaving 1.06g (99%) crude oil-white product. Recrystallization in methanol followed by sublimation yielded pure white crystals.

Melting Point: 123.6-123.9°C. Literature [15] 124-125°C.

Elemental Analysis (%) Calculated for  $C_{14}H_{12}O$ : C 90.35, H 5.65. (Found) C 90.35, H 5.65.

$^1H$  NMR ( $\delta$ ): 7.30 s, 1.15-1.65 m. Literature [16] 7.15 s, 1.25-1.50.

#### Synthesis of the Model Compound Triis-1,2,3,4,5-pentabenzene

A solution of freshly distilled 3-benzofuran (1.8 ml, 12 mmol) in 30 ml of dry THF was added into the reaction flask containing the zwitteric complex and refluxed for one hour (while still maintaining an argon atmosphere). After cooling to room temperature, approximately 60 ml of petroleum ether was added causing a massive black precipitate to cling to the walls of the flask. A cloudy yellow solvent-soluble which was easily poured was a filter. The black residue, which consists of inorganic salts, tars and unreacted zinc was retained in the reaction vessel, where it was washed with petroleum ether. Although the black residue was still an irritant at this point, no problem was encountered in exposing the black material to the air during the washing procedure. The two fractions were combined, placed in a rotary evaporator and the solvent removed, resulting in 0.96g (99%) crude oil-brown solid which was recrystallized in methanol and sublimed to yield large light yellow crystals.

Melting Point: 76.5-77.8°C. Literature [23] 140°C.

Elemental Analysis (%) Calculated for  $C_{13}H_8O$ : C 73.05, H 3.60. (Found) C 74.85, H 3.35.

<sup>1</sup>H NMR (CD<sub>3</sub>) 4.30-6.1, 6.42-6.6, 6.83-6.1, 7.39-6.1, aromatic (2H) 4.25, 4.50, 4.76, 7.28

<sup>13</sup>C NMR (CD<sub>3</sub>) 108.7, 111.3, 134-9, 142.3, 152-9

#### Synthesis of the Model Compound From 1,2-di(2-ethylhexyloxy)ethane

A solution of freshly distilled 2-diethylhexyloxyethanol (I) (2 and 12 mmol) in 10 ml of dry THF was syringed into the reaction flask containing the reductive complex and refluxed for two hours (while still maintaining an argon atmosphere). After cooling to room temperature, approximately 60 ml of petroleum ether was added causing a viscous black precipitate to form in the walls of the flask. A cloudy yellow solution resulted which was easily poured into a filter. The black residue, which consists of mercury, silver, arsenic, and unreacted zinc was retained in the reaction vessel, where it was washed with petroleum ether. Although the black residue was still not removed at this point, no problem was encountered in exposing the black material to the air during the washing procedure. The two fractions were combined, placed on a rotary evaporator and the solvent removed, resulting in 1.08 g (44%) crude yellow solid which was recrystallized in methanol and subjected to yield small white crystals.

Melting Point: 138 °C, literature [36] 128-131 °C

Elemental Analysis (%) (calculated for C<sub>22</sub>H<sub>42</sub>O<sub>2</sub>) C 82.35, H-6.17 (found) C 82.36, H-6.13

<sup>1</sup>H NMR (CD<sub>3</sub>) 4.99-7.05 m, 5.07 s, 7.19 d, aromatic (2H) 4.66 s 3.33 m (overlapping olefinic).

<sup>13</sup>C NMR (CD<sub>3</sub>) 123.4, 124.3, 125.9, 127.6, 142.3

#### Synthesis of the Model Compound From 1,2-di(2-ethylhexyloxy)ethane

A solution of freshly distilled 2-ethylhexanol (I) (2 and 12 mmol) in 10 ml of dry THF was syringed into the reaction flask containing the reductive complex and refluxed for two hours (while still maintaining an argon atmosphere). After cooling to room temperature, approximately 60 ml of petroleum ether was added causing a viscous black precipitate to form in the walls of the flask. A cloudy red solution resulted which was easily poured into

a filter. The black residue, which consists of inorganic salts, titanium, and unreacted zinc was retained in the reaction vessel, where it was washed with petroleum ether. Although the black residue was still air sensitive at this point, no problem was encountered in exposing the black material to the air during the washing procedure. The two fractions were combined, placed on a rotary evaporator and the solvent removed, resulting in 0.83 g (24%) crude red brown solid. Sublimation yielded clear crystals.

Boiling Point: 179-180°C, literature [26] 176-177°C

Elemental Analysis (%) (calculated for  $C_{22}H_{12}O_2$ ) C 75.00, H-3.00; found: C-74.18, H-3.08

$^1H$  NMR ( $\delta$ ): 6.62 d, 6.68 + 7.42 s, 7.52 m; literature [26] 6.52 m, 6.60 s, 7.12 m, 7.44 m

$^{13}C$  NMR ( $\delta$ ): 166.3, 171.2, 123-4, 128.3, 142.3

### Trans-1,2-dichloroanthracene

Freshly distilled 3-thiophenecarboxaldehyde (1.05 ml, 11 mmole) in 70 ml of dry THF was injected into the reaction flask containing the catalytic complex and allowed for 2 hours (while still maintaining an argon atmosphere). After cooling to room temperature, approximately 60 ml of petroleum ether was added causing a viscous black precipitate to cling to the walls of the flask. A cloudy yellow solution resulted which was easily poured into a filter. The black residue, which consists of inorganic salts, titanium, and unreacted zinc was retained in the reaction vessel, where it was washed with petroleum ether. Although the black material was still air sensitive at this point, no problem was encountered in exposing the black material to the air during the washing procedure. The two fractions were combined, placed on a rotary evaporator and the solvent removed, resulting in 1.09 g (24%) crude yellowish solid. Recrystallization or reprecipitation followed with ethanol as yielded a light yellow crystalline powder.

Melting Point: 145-150°C, literature [26] 148-150°C.

Elemental Analysis (%) : Isolated for  $C_{12}H_{10}N_2O_2$  C 68.58, H 4.17, (found) C 68.83, H 4.48

$^1H$  NMR ( $\delta$ ) : 8.97 s, 7.33 s, 7.31 s, literature [26] 7.90 s, 7.25 s.

$^{13}C$  NMR ( $\delta$ ) : 131.3, 131.4, 134.3, 135.0, 139.8.

### Isomericism via Thermally Reversible Self-Gravel

#### The Synthesis-Coupling of *p*-Terephthaloylchloride with Ethylenediols

The purpose of this reaction was to investigate the feasibility of coupling an aromatic dihalide possessing a 1-hydroxycarbonyloxy side group. Preparation of the starting compound *p*-tert-butoxycarbonyloxycarbonylchloride proceeded as follows [27].

A solution of 5.4 g *p*-hydroxycarbonylchloride in 100 ml of dry THF was mixed with 5.6 g potassium carbonate under argon. After reacting for a few minutes at room temperature, *tert*-butoxycarbonylchloride (10.7 g, 13.34 ml) was added and the mixture stirred for one hour. The mixture was poured over 300 ml crushed ice and the product extracted with ethyl acetate. This solution was washed with water several times and dried over anhydrous magnesium sulfate. After solvent removal 9.45 g of crude light-yellow product was obtained. The crude product was washed with hexane, yielding 3.64 g of white crystalline powder.

Melting Point: 70-80°C

$^1H$  NMR ( $\delta$ ) : 1.27 s, 7.35 d, 7.65 d, 9.94 s, literature [27] 1.27 s, 7.26, 7.39, 7.76, 7.94

A solution of the *p*-tert-butoxycarbonyloxycarbonylchloride (2.60 g, 13 mmol) in 50 ml of dry THF was exposed over the flask containing the solution complex and refluxed for 2 hours (while still maintaining an argon atmosphere). After cooling to room temperature, approximately 60 ml of potassium ether was added causing a viscous black precipitate to cling to the walls of the flask. A cloudy white solution resulted which was easily poured into a filter. The black residue, which consists of inorganic salts, tars, and unreacted

was suspended in the reaction vessel, where it was washed with petroleum ether. Although the black residue was still not removed at this point, no problem was encountered in exposing the black material to the air during the washing procedure. The two fractions were combined, placed on a rotary evaporator and the solvent removed, resulting in 1.11 g (40%) off-white solid. Characterization by elemental analysis and NMR revealed that the t-BOC group had not survived the coupling process, resulting in formation of  $\alpha,\beta$ - $\gamma$ -hydroxyketones.

Melting Point: >200°C decomposition.

Elemental Analysis (%) (calculated for  $C_{14}H_{17}O_3$ ) C 79.24, H 8.56, (found) C 79.05, H 8.70

$^1H$  NMR ( $\delta$ ) = 4.49 s, 4.43 d, 1.4 d, 0.58 s

$^{13}C$  NMR ( $\delta$ ) = 115.9, 120.1, 127.1, 128.4, 136.8

### Model Compound Preparation

#### Synthesis of the Model Compound 1,2-Dioxane-3,4-Diethanol

Although tetrahydrofuran had been previously synthesized by Mukaiyama et al. (8), the reaction was repeated for the purpose of verifying their results. A modification, however, was necessary to obtain near quantitative yields. This modification involved forming the solvate-complex with sulfur before addition of the aldehyde or ketone. As a result of this change, superior yields were obtained in almost every case.

For this reaction, a solution of freshly distilled tetrahydrofuran (1.2 ml (15 mmole)) in 10 ml of dry THF was injected into the reaction flask containing the solvate complex, which had been cooled to 0°C using an ice bath. The reaction was stirred for two hours under a stream of argon, while the temperature was maintained at 0°C. A potassium carbonate solution (10%, 1.66 ml) is added to the reaction resulting in a precipitated solid and a slight evolution of heat. This mixture was allowed to stir for an additional two hours while remaining in the ice bath. Afterwards the suspension was

vacuum filtered and the filtrate extracted twice with 100-ml diethyl ether. The filter cake was also washed with 50 ml of diethyl ether, which was added to the other two fractions. After the ether solution had been dried over anhydrous magnesium sulfate and filtered, the solvent was removed by rotary evaporator yielding 1.24 g (97%) off-white powder. White crystals were obtained with recrystallization in diethyl ether/petroleum ether mixture.

**Melting Point:** (crude) off-white) 113-6°C, (pure - crude) 113°C; (crude) (10) (4 and 5) 145.5-148.2°C, (28) (30) 120°C, (crude) 117°C.

**Elemental Analysis (%)** (calculated for  $C_{12}H_{14}O_2$ ) C-78.55, H-5.61, (found) C-78.12, H-5.58

**$^1H$  NMR ( $\delta$ ):** (dimethyl) 2.4-5 (D<sub>2</sub>O exchange), 4.35-m, 7.2-m, (crude) 2.2-s, 4.87-s, 3.5-s, (crude) (10) (crude) 2.4 (D<sub>2</sub>O exchange), 4.84-s, 7.1-7.3-m, (30) 2.8s, 4-4.5s, 7.0-7.3-m

### **Synthesis of the Model Compound 1,3-Dibenzyl-2-ethanolol**

A solution of freshly distilled 2-benzylol (1.0 ml 12 mmol) in 10-ml of dry THF was stirred into the reaction flask containing the complex, which had been cooled to 0°C with an ice bath. The reaction was stirred for one hour under a stream of argon, while the temperature was maintained at 0°C. A potassium carbonate solution (10%, 100 ml) is added to the reaction resulting in a precipitate of inorganic salts and a slight evolution of heat. This mixture was allowed to stir for an additional two hours while remaining in the ice bath. Afterwards the suspension was vacuum filtered and the filtrate extracted twice with 100-ml diethyl ether. The filter cake was also washed with 50 ml of diethyl ether which was added to the other two fractions. After the ether solution had been dried over anhydrous magnesium sulfate and filtered, the solvent was removed by rotary evaporator yielding 1.36 g (91%) of dark yellow oil. The crude product was purified using a silica column with ether as the eluent.

**Elemental Analysis (%)** (calculated for  $C_{12}H_{10}O_2$ ) C 86.16, H 4.83; (found) C 87.11, H 4.79

$^1H$  NMR ( $\delta$ ): 2.6 s, 3.0 m, 4.3 m, 7.4 s.

### Synthesis of the Model Compound 1,3-Diphenyl-1,3-ethanediol

A solution of freshly distilled 2-naphthencarbonalddehyde (1.33 ml, 11 mmol) in 80 ml dry THF was injected into the reaction flask containing the reductive complex, which had been cooled to  $0^\circ C$  with an ice bath. The reaction was started for two hours under a stream of argon, while the temperature was maintained at  $0^\circ C$ . A potassium carbonate solution (10%, 80 ml) is added to the reaction resulting in a precipitation of inorganic salt and a slight evolution of heat. The mixture was allowed to stir for an additional two hours while remaining in the ice bath. Afterwards the suspension was carefully filtered and the filtrate extracted twice with 100 ml diethyl ether. The ether extract was also washed with 50 ml of diethyl ether which was added to the other two fractions. After the ether solutions had been dried over anhydrous magnesium sulfate and filtered, the solvent was removed by rotary evaporation, yielding 1.36 g (quantitative yield) of cream-colored oil. The crude product was purified in one step by using a silica column with ether as the eluent.

**Elemental Analysis (%)** (calculated for  $C_{12}H_{12}O_2$ ) C 83.16, H 6.62; (found) C 83.91, H 6.51

$^1H$  NMR ( $\delta$ ): 2.6 s, 3.35 s, 5.0 s, 7.1 s, 6.8 m, 7.25 m.

### Reagents and the Coupling Mechanism

#### Synthesis of Achromic Ketyl Using 1-Naphthol and 2,3,5-Trinitrobenzoic Acid

The kethanide which is most chosen for the model compound study was m(3-methoxyphenylphenylmethyl)-d-coupleran(II). For the model compound 1,3-diphenyl-1,3-ethanediol, the original NMR sample consisted of approximately 20 mg of the diol dissolved in 0.5 ml of Solvent C (deuterated chloroform with 1% TMS), from which a base spectrum was obtained. After acquisition of the base spectrum, 1 mg of the kethanide reagent was added directly to the NMR sample vial.

separately, and a second spectrum obtained. A third spectrum was obtained after the addition of another 4 mg of the reagents again.

$^1\text{H}$  NMR ( $\delta$ ) - hexa spectrum. (Solvent) 2.6-6, 4.7 m, 7.2 m.

$^1\text{H}$  NMR ( $\delta$ ) - 2 mg shell reagent. (Solvent) 3.2 u, 4.8 u, 4.9 u, 7.2 m.

$^1\text{H}$  NMR ( $\delta$ ) - 6 mg shell reagent. (Solvent) 3.2 u, 4.9 u, 5.5 u, 7.3 m.

For the model compound 1,2-dithienyl-1,2-ethanediol, the original NMR sample contained of approximately 25 mg of the salt dissolved in 0.5 ml of DMSO- $d_6$  from which a hexa spectrum was obtained. After acquisition of the hexa spectrum, 6 mg of the hexamethyl reagent was added directly to the NMR sample, shaken vigorously, and a second spectrum obtained.

$^1\text{H}$  NMR ( $\delta$ ) - hexa spectrum: 1.8 u, 3.25 u, 3.6 u, 5.6 u, 6.7 m, 7.15 m.

$^1\text{H}$  NMR ( $\delta$ ) - 6 mg shell reagent: 3.4 u, 4.15 u, 7.1 m, 7.3 m.

#### General Procedure for the Synthesis of 1,2-Dithienyl-1,2-ethanediol

The synthesis of 1,2-dithienyl-1,2-ethanediol was performed twice, with the first reaction involving hydrolysis with  $\text{H}_2\text{O}$ .  $\text{H}_2\text{O}$ -labeled water (purchased from MSD Isotopes) to trace possible incorporation of water oxygen into the final product. Due to the expense of this reagent, the acetal coupling reaction of hexamethylenediol was undertaken such that it could be performed in a 25 ml 3-necked flask [19]. The  $\text{TiCl}_4$  (33 ml, 3 mmole) was added to the acid powder (2.4 g, 6 mmole) in 5 ml of dry THF, which had been cooled to  $-10^\circ\text{C}$ . A solution of freshly distilled hexamethylenediol (30.0 ml, 240 mg, 3 mmole) in 5 ml of dry THF was added and the reaction stirred for 45 minutes. The color of the reaction proceeded through the usual transition of green to purple to dark brown.

The  $\text{H}_2\text{O}$ -labeled water (8.5 ml) was mixed with 8.1 g of potassium carbonate to form a saturated solution, decanted off and added to the reaction mixture. The color darkened to blue-black. The reaction mixture was diluted with distilled ether, filtered through celite, and washed with a sodium chloride solution. After drying over magnesium sulfate, the ether was removed by a rotary evaporator, yielding 1.65 g (39%) crude white

product. The 1,3-dithioph-4,5-dithiol was recrystallized in an ether / petroleum ether solvent and analyzed by mass spectrometry.

In the second reaction the exact same procedure was followed, except that non-labeled disuccinic anhydride was used during the hydrolysis step, yielding 3.08 g (94%) crude white product. Recrystallization was again carried out in an ether / petroleum ether solvent and the resulting crystals analyzed by mass spectrometry.

Mass Spectrum : reaction 1 : (static probe, EI, 70 ev. m/z) 214 parent (m/z 100), 108, 107, 76, 77

Mass Spectrum : reaction 2 : (static probe, EI, 70 ev. m/z) 214 parent, 108 (65), 76, 77

### Polymerization of Dithiobutyric acid, $\text{DCl}_4 \cdot 2\text{H}_2\text{O}$

#### Polymerization of Terephthalic acid to Poly(LA-4-thiobutyric acid)

A solution of freshly sublimed terephthalic acid (2.0 g, 6 mmol) in 10 ml of dry THF was injected into the solution vial and refluxed for 18 hours. After allowing the reaction to cool, 100 ml of 10% potassium carbonate solution was added to the reaction and stirred for 30 minutes. After filtration, the white / THF layer and filter cake were washed with several fractions of diethyl ether. The ether was dried over anhydrous  $\text{CaH}_2$  and removed by a rotary evaporator leaving behind trace amounts of a yellow oil. No starting compound was isolated.

The solid filter cake was placed in a flask with 100 ml of DMF and refluxed for several hours, causing the solution to become fluorescent yellow. After filtration, the solution was slowly dropped into several hundred milliliters of water resulting in precipitation of a yellow solid, highly contaminated with inorganic salts. Purification of the polymer was accomplished by refluxing in DMF followed by reprecipitation again in water, yielding a yellow beaded film after filtration. The polymer was still found to be contaminated, based on elemental analysis results. An atropisomeric  $^{13}\text{C}$  NMR spectrum was not obtained due to the low solubility of the polymer. Solid state  $^{13}\text{C}$  was performed using

a solid) were preheated by Dery Scientific Incorporated, but lower yields of the resulting specimens were not found in the actual run.

Melting Point: decomposes > 300°C

Elemental Analysis (%) (calculated for  $C_{16}H_{12}$ ) C 94.31, H 5.69 (found) C 90.65, H 5.73

$^1H$  NMR ( $\delta$ ): 6.3-6.7 m.

IR (KBr,  $\mu$ ): 3300 (weak, C-H stretch), 1630 (strong, C=C stretch), 1000 (weak), 815 (weak)

Molecular Weight ( $M_n$ ): 1000 (end group analysis)

### Attempted Polymerization of 1,2-Dibenzylindylene in the Polycondensate

The monomer was prepared by reduction of 1,2-dibenzylindylene with tin amalgam (2%). To a flask containing 10 g of mercuric chloride and 100 ml of deionized water was added 100 g of 30-mesh tin metal. The flask was stoppered and shaken until all of the tin appeared to have a dull silvery coating. The tin amalgam was then washed repeatedly with water until the washings were nearly clear.

The tin amalgam (100 g) was added to 1,2-dibenzylindylene (5.0 g) in 100 ml of 95% ethanol. The mixture was heated to reflux dissolving the dione, and leaving a clear yellow solution with the metal. Concentrated HCl (20 ml) was slowly added. After five minutes of reflux the solution became colorless. The metal was filtered off while the mixture was still hot. As the solution cooled to room temperature, 3.0 g (20%) yellow needle-like crystals precipitated out, which were recrystallized in methanol.

Melting Point: 143-4°C. Literature (2%) 146°C.

$^1H$  NMR ( $\delta$ ): 3.3 s, 7.3 m, 8.0 m.

A solution of the 1,2-dibenzylindylene (1.60 g, 5 mmol) in 50 ml of dry THF was injected into the reduction-complex and refluxed for 10 hours. After allowing the reaction to cool, 100 ml of a potassium-tuboxate solution was added to the reaction and stirred for 30 minutes. After filtration the water/THF layer and filter cake were washed with several

fraction of diethyl ether. The ether was dried over magnesium sulfate and removed by a rotary evaporator yielding 0-07 g (31%) of an off-yellow solid. The product was purified by a silica gel column using petroleum ether as an eluent producing yellow crystals.

Characterization of this compound revealed that coupling had occurred intramolecularly resulting in the cyclized product, 1,2-diphenylcyclobutane.

Melting Point: 49.3-50.0°C; literature [22] 50.3-51.0°C.

Elemental Analysis (%) Calculated for  $C_{12}H_{10}$ : C 91.26, H 4.93, (found) C 90.65, H 4.83.

$^1H$  NMR ( $CDCl_3$ ): 2.13 s, 4.16 T 20°; literature [22] 2.10 s, 2.15-3.65 m.

#### Attempted Polymerization of Dichlorodifluoro-1,2-bisphenylpropanes

A solution of 1,2-dichlorodifluoro-1,2-bisphenylpropane (1.50 g, 4 mmol) in 10 ml of dry THF was exposed into the flask containing the reduction complex and refluxed for 18 hours. After allowing the reaction to cool, 100 ml of 10% potassium carbonate solution was added to the mixture and stirred for 30 minutes. After filtration, the water/THF layer and filter cake were washed with several fractions of diethyl ether. The ether was dried over magnesium sulfate and removed by rotary evaporator yielding a yellow oil.

In an attempt to isolate higher molecular weight product, the thin film residue was placed in a Soxhlet extractor with THF and refluxed for two days yielding a more viscous yellow oil. DMF was then placed in the extractor with the film cake and refluxed for 14 hours, yielding only undetectable impurities. Although the proton NMR spectrum of the oil gave the expected resonances for a highly conjugated phenyl compound, high molecular weight polymer could not be isolated.

$^1H$  NMR of yellow oil (2): 6.8-7.8 m.

#### Attempted Polymerization of 1,2-Dichlorodifluoro-1,2-bisphenyl(2,2,4,4-tetrafluoroethyl)

The monomer for this reaction was synthesized by the oxidation of 3-hydroxy-2-methyl-2-butanol with lead acetate (20). A solution of pyridine (10 ml, distilled from calcium hydride) and 3-hydroxy-2-methyl-2-butanol (9.34 g, 34 mmol) was cooled to 0°C in an

ice bath. The lead acetate (33.7 g, 45 mmol) was added with stirring raising the temperature to just to 25°C. After 10 minutes the ice bath was removed and the stirring continued for three hours. During this time the temperature rose to around 35°C and the mixture became a clear yellow solution. After an hour the temperature dropped and a off white solid precipitated.

When the three hours were completed, the mixture was poured into 200 ml of ice water and acidified with 10% HCl. The resulting suspension was filtered and the filtrate extracted with diethyl ether. The resulting cake was also washed with diethyl ether. The two fractions were then combined, washed with a saturated sodium bicarbonate solution, dried over anhydrous magnesium sulfate and evaporated to yield 7 g (76%) of crude 2,3-dicarbonylthiophene, which was recrystallised in carbon tetrachloride. Sublimation at full vacuum and 70-80°C yielded 4.5 g (46%) of pure white product.

Boiling Point: 128-9°C; literature [30] 135-137°C.

<sup>1</sup>H NMR (d<sub>6</sub>) 7.35 s, 9.9 s; literature [30] 7.36 s; 9.86 s

<sup>13</sup>C NMR (d<sub>6</sub>) 119.3, 134.3, 139.2

A solution of the 2,3-dicarbonylthiophene (5.62 g, 9 mmole) in 50 ml of THF was injected into the reaction flask containing the solution complex and refluxed for 10 hours. After allowing the mixture to cool, 30 ml of a potassium carbonate solution was added to the reaction and stirred for 10 minutes. After filtration, the water / THF layer and filter cake were washed with several fractions of diethyl ether. The ether was dried over magnesium sulfate and removed by a rotary evaporator pulling a vacuum ml. Visual inspection of the filter cake revealed the presence of small amounts colored flakes which were believed to be polymer, but every attempt to separate them from the composite cake proved unsuccessful.

### Polymerization of Decaphthaldehyde to Poly(1,4-phenylene-1,2-ethynylene)

A solution of freshly sublimed decaphthaldehyde (8.6 g, 0.04 mmole) in 10 ml of dry THF was injected into the solution complex, which had been cooled to 0°C with an ice bath. The temperature was carefully maintained at 0°C while the mixture stirred for 10 hours, after which it was hydrolyzed with a 10% potassium carbonate solution, stirred for five additional hours and filtered. The lower molecular weight fraction of the polymer was isolated by removal of the water / THF solvent mixture. The higher molecular weight fraction was isolated by refluxing the filter cake in THF for four hours, followed by filtration and solvent removal. The off white polymer was purified by reprecipitation in hexane.

Melting Point: solvent/96-110°C, decomposes > 180°C

Elemental Analysis (%): (calculated for  $C_{24}H_{12}O_2$ ) C-90.59 H-5.89, (found) C-89.64 H-6.65

$^1H$  NMR ( $\delta$ ): 4.3-5.3 m, 3.3-3.8 m, 4.3-4.8 m, 5.9 m

$^{13}C$  NMR ( $\delta$ ): 76-5, 78.6, 125.6, 126.6, 127.0, 141.0

IR (KBr,  $\mu$ ): 3400 (broad, O-H stretch), 2840 (aromatic, C-H stretch), 1700 (weak, C=O stretch), 1600 (weak, C=C stretch), 1280 (strong), 1088 (strong)

Molecular Weight ( $M_n$ ): 3850 (end group analysis), 3680 (GPC)

### Polymerization of 1,2-Fluorodecaphthaldehyde to Poly(1,4-phenylene-1,2-ethynylene)

A solution of 1,2-fluorodecaphthaldehyde (8.6 g, 0.04 mmole) in 10 ml of THF was injected into the reaction flask containing the solution complex which had been cooled to 0°C with an ice bath. The temperature was carefully maintained at 0°C while the mixture stirred for 10 hours, after which it was hydrolyzed with a 10% potassium carbonate solution, stirred for five additional hours and filtered. The lower molecular weight fraction of the polymer was isolated as a mixture and by removal of the water / THF solvent mixture. The higher molecular weight fraction was isolated as a brittle dark red solid by refluxing the filter cake in THF for four hours, followed by filtration and solvent removal.

Melting Point: decomposes > 350°C.

Elemental Analysis (%) (calculated for  $C_{21}H_{14}O_2$ ) C 81.14, H 4.76% (found) C 81.01, H 4.76%

$^1H$  NMR ( $CDCl_3$ ): 4.0-4.7 m, 4.7-5.9 m, 6.0-6.8 m, 7.4 s, 12.0 m

IR ( $CDCl_3$ ,  $\mu$ ): 3400 (strong, O-H stretch), 2900 (strong, C-H stretch), 1710 (weak, C=O), 1530 (weak), 1010 (strong)

Molecular Weight ( $M_n$ ): 3340 (end-group analysis).

### Molecular Weight Analysis by Vapor Pressure Osmometry

With the vapor pressure osmometer small differences in vapor pressure between a pure solvent and a solution are converted to temperature differences which can be measured very precisely with thermistors. When calibrated with a suitable standard material, the temperature difference can be converted to a concentration and then to molecular weight.

### Calibration of Instrument Using Beesil as Standard

The output of the instrument was 50 microcentipoise with an operating temperature of 105°C. Three solutions of beesil in DMSO were made of varying concentrations. An average  $\Delta T$  for each standard solution was obtained and divided by the concentration of the solution. These values were plotted versus concentration and the best fit straight line extrapolated to zero concentration. Multiplying this intercept value by the molecular weight of beesil (316) yielded a calibration factor K of 444 which could then be used to calculate the molecular weight of the polymer sample.

Table 2.1 Data from VPO measurements of beesil standards

Standard concentration	$\Delta T$	$\Delta T/C$
2.40 g/l	1.87	1.24
4.30 g/l	5.83	1.34
8.08 g/l	30.1	2.46

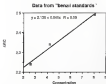


Figure 3-1 Plot of data from benzal standards used to determine calibration constant.

### Polymer Sample Measurements

Four solutions of poly[1,4-phenylene-1,2-ethylenedio] in DMSO were made of varying concentrations. An average  $\Delta T$  for each solution was again observed and the value divided by its concentration and plotted versus concentration. The resulting intercept value was then divided into the calibration factor  $K$  to yield a number average molecular weight value of 2560 for the polymer.

Table 3-3 Data from VPO measurements of poly[phenylene-ethylenedio]

Standard concentration	$\Delta T$	$\Delta T/C$
0.79 $\mu\text{g}$	0.83	1.16
1.57 $\mu\text{g}$	1.74	1.11
1.81 $\mu\text{g}$	2.16	1.20
1.94 $\mu\text{g}$	2.26	1.16

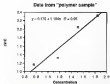


Figure 3-3. Plot of data from polymer solutions used to calculate molecular weight.

## CHAPTER 3 MODEL COMPOUND STUDIES OF THE MIKAYAMA-COUPPLING SYSTEM

A model compound study was conducted to evaluate the utility of the Mikayama system for the coupling of carbonyls, as better understood as application to the synthesis of polymers. Although Mikayama and coworkers (8) reported near quantitative yields for aromatic aldehydes and ketones, it was necessary to verify these yields for both aldehydes and ketone reactions, as well as assess the validity of extending this chemistry to hetero-aromatic aldehydes. In this research, single crystal X-ray studies of olefin models allowed unequivocal structural assignments to be made and yielded valuable information into the requirements for polymer chain planarity. A prediction of regularity in polyunsaturation was made possible by extrapolation of the general model's using proton NMR and isotopic labeling techniques, yielding valuable information concerning steric hindrance, as well as further details into the reaction mechanism.

### Coupling of Heteroaromatic Aldehydes to Olefins

To verify the results of Mikayama et al.(8), the synthesis of sulfone was repeated following his procedure for olefin formation (Figure 3-1). This process involved the slow addition of a suspension of wax powder in dioxane to a solution of sodium methoxide and benzaldehyde in dioxane at  $-10^{\circ}\text{C}$  under argon. This procedure proved to be awkward at first, since addition of the wax powder was difficult while maintaining the inert atmosphere. After refluxing the reaction mixture for 4 hr, the mixture was quenched with 10% aqueous calcium acetate followed by ether extraction. Unlike the near quantitative yields observed by Mikayama, actual isolated yields using this procedure were only about 70%.

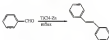


Figure 3-1. Coupling of benzaldehyde to form stilbene

Modifications of the Ishiyama procedure involved a change in the reagent addition order.  $\text{TiCl}_4$  was added carefully to a mixture of zinc powder and benzaldehyde in toluene allowing for a quicker and cleaner addition process. Yield improved substantially to approximately 90% isolated product.

The best results, however, were obtained by a combination of procedures used by McMurry (Finning) [14] and Cox [31], which involved two important modifications. First the  $\text{TiCl}_4/\text{Zn}$  complex was formed in THF prior to the addition of the aldehyde. Specifically  $\text{TiCl}_4$  was added carefully to a suspension of zinc powder in THF at  $-10^\circ\text{C}$  under argon, then refluxed for one hour resulting in a slow color change from yellow to blue black. After the complex cooled to room temperature benzaldehyde was added, and the mixture refluxed for an additional two hours. By refluxing the complex separately prior to the addition of reagent, a more reactive low-valent titanium species, possibly  $\text{Ti(0)}$ , is claimed to form [12, 30]. The second modification involved a change in the work-up procedure. Instead of quenching the reaction with a 10% potassium carbonate solution, the mixture was diluted with petroleum ether causing a viscous black precipitate to cling to the walls of the flask. A cloudy white solution resulted which was easily decanted, leaving behind the black impurity residue. By implementing these modifications, yields for the formation of stilbene and other model alkenes approached near quantitative levels.

After an experimental procedure had been developed to give reproducible results with high yields, attempts were made at coupling heterocyclic aldehydes (see

synthesizing such model compounds provides valuable insight into the possibility of making tertiary chemistry for the synthesis of poly(heterocyclicarylene)s.

2-Furaland 2-thiophenecarbaldehyde were coupled using the modified Mukaiyama procedure and yielded the dienes, 1,2-di(2-furyl)ethylene and 1,2-di(2-thiophenyl)ethylene as crystalline solids in high yields: 99% and 94% respectively (Figure 3-1). NMR characterization of the crude product showed that in each case, the *cis*-diene was synthesized almost exclusively (Spectra 3-1 through 3-4). This observation is in agreement with Mukaiyama's synthesis of stilbene, which was found to be in a 99% *cis* configuration[4].

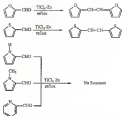
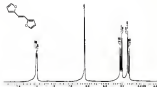
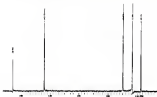


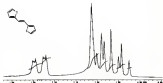
Figure 3-1 Coupling of heterocyclic aldehydes to the respective diene compound.



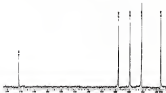
Spectrum S-1. <sup>1</sup>H NMR spectrum of 1,3-di(2-furyl)butylene.



Spectrum S-2. <sup>13</sup>C NMR spectrum of 1,3-di(2-furyl)butylene.



Spectrum 3-3:  $^1\text{H}$  NMR spectrum of 1,2-dicyanobenzene.



Spectrum 3-4:  $^{13}\text{C}$  NMR spectrum of 1,2-dicyanobenzene.

2-Pyridinecarboxaldehyde was the next heterocycle to be investigated. Unlike the furan and thiophene analogs, however, no appreciable diolfin product was obtained. Instead a black tar was isolated which appeared to be polymeric in nature. It was initially believed that the inability of the pyridine compound to couple is a result of the proton on nitrogen acting as an acid and destroying the complex. This hypothesis was discarded when 1-methyl-2-pyridinecarboxaldehyde and 2-pyridinecarboxaldehyde both failed to couple to the corresponding diolfin. The reason for the lack of coupling in the nitrogen-containing heterocycles appears to be an interaction between the lone pair of electrons on nitrogen and the complex preventing proper reduction of the carbonyl. This result is corroborated by Ceresa and Porto [28] who found that an amine group placed on the ring of acetylphenone prevents coupling of the carbonyl to aqueous  $TiCl_3$  yet allows its reduction to the corresponding alcohol. Thomas and Schwenk [29] similarly found that nitrogen got reacted with their  $TiCl_3$  pig system as form an unstable complex. This observation led to the use of organotin compounds as subsequent heterocycle reactions.

### Key Structural Determinants of Heterocycle Diolfin

Requirements for conductivity include extensive  $\pi$ -orbital overlap along the polymer backbone as well as a morphology allowing large intermolecular interactions and an optimum solid state order [23]. These requirements are dependent on the extent of conjugated ring twist found within the polymer structure as well as the regularity of configuration within the repeat unit, and the larger the internal ring angle the smaller the extent of  $\pi$ -orbital overlap, reducing conductivity. In addition, regularity of configuration within the repeat unit is important in allowing the morphology necessary for the intermolecular interaction. However, due to the unavailability of these polymers much information concerning their structure and order must come from a study of model compounds.

Consequently, study of the heterocyclic olefin derivatives of cellulose as model compounds was undertaken employing single crystal X-ray structural analysis to elucidate various ring conformations. Rowan and coworkers [57] demonstrated that the phenyl rings in single crystal neat cellulose have a molecular plane ring twist of over  $3^\circ$ , due to steric interaction between the vinyl protons and the ortho protons on the phenyl rings (Figure 3-3).



Figure 3-3. Steric interaction found in neat cellulose by Rowan et al.

In order to obtain comparative values for the model compound study in this discussion, X-ray analysis was performed on single crystals of 1,2-d(3)-furylcellulose and 1,2-d(3)-thierylcellulose. In the case of the disulfone analog, the ring twist is  $4.4^\circ$ , which is nearly 50% more planar than the cellulose molecule analyzed by Rowan and coworkers. With the disulfone version, the phenyl ring twist is only  $1.1^\circ$ , indicating an almost coplanar structure. In addition, the hydrogen in both cases is turned in toward the double bond (Figure 3-4).

To elucidate the reasons for these observations, the hydrogen was forced away from the double bond by synthesizing neat 1,2-d(3)-furylcellulose and neat 1,2-d(3)-thierylcellulose, via McPherson chemistry. In doing so, a proton on the heterocyclic ring is forced to interact with the vinyl protons, and X-ray analysis of the latter analog revealed a fivefold increase in the torsional ring twist to  $5.0^\circ$  (Figure 3-5). By forcing this interaction

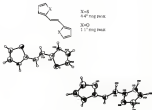


Figure 3-4 X-ray structures of *trans*-1,2-difluoro-1,2-diphenylethane and 1,2-difluoro-1,2-diphenylpropane



Figure 3-5 X-ray structure of *trans*-1,2-difluoro-1,2-diphenylpropane

turned in toward the double bond, the attraction between the vinyl protons and the ring protons is weakened, resulting in a more planar configuration.

Another interesting observation is the amount of torsional ring distortion which exists within the various heterocyclic systems. Table 3-1 shows that within most of 1,2-dialkylbenzylidenes, as one moves around the ring, the torsional bond angles vary from  $-3.0^\circ$  to  $+3.4^\circ$ . In the case of 1,2-dialkylbenzylidenes, the rings exhibit a much smaller distortion range of  $-1.4^\circ$  to  $0.4^\circ$  (Table 3-2). However, if one examines the same torsional bond angles of 1,2-dialkylbenzylidenes (Table 3-3), one finds that the distortion has increased to a range of  $-2.5^\circ$  to  $2.5^\circ$ .

Table 3-1 Torsional bond angles of some 1,2-dialkyl benzylidenes

C-C(4)-C(3)-C(2)	+1.8°
C-C(3)-C(2)-C(1)	+1.5°
C(4)-C-C(1)-C(2)	-0.8°
C(3)-C-C(4)-C(2)	-0.8°
C(3)-C(2)-C(1)-C(4)	-2.6°

Table 3-2 Torsional bond angles of some 1,2-dialkylbenzylidenes

C(5)-C(4)-C(3)-C(2)	+0.8°
C(2)-C(1)-C(2)-C(3)	+0.8°
C(4)-C(1)-C(2)-C(3)	-0.4°
C(1)-C(2)-C(3)-C(4)	-0.4°
C(1)-C(2)-C(3)-C(4)	-0.4°

Table 3-3 Torsional bond angles of some 1,2-dialkylbenzylidenes

C-C(4)-C(3)-C(2)	+0.0°
C-C(3)-C(2)-C(1)	+2.5°
C(4)-C-C(3)-C(2)	+1.5°
C(3)-C-C(4)-C(2)	+1.4°
C(3)-C(2)-C(1)-C(4)	1.2°

Comparing the single-crystal data of the heterocyclic dienes prepared with McMurtry chemistry to Brown's work with silole allows one to make predictions concerning their respective polymers. Poly(phospholethiophene) would not be planar but would possess a significant ring twist, due to the steric interactions of protons, reducing the extent of  $\pi$  overlap along the conjugated backbone. The poly(heterocyclethiophene)s would tend to be more flat, with poly(2,5-furylthiophene) approaching a near coplanar conformation, resulting in greater  $\pi$  overlap and higher conductivity.

Observing the heterocycle located in *gauche* around the double bond suggests that the poly(heterocyclethiophene) would have a regular configuration from repeat unit to repeat unit. This characteristic is very important for conductivity, since it should permit chains to pack more closely, increasing intermolecular interaction of  $\pi$ -orbitals. Figure 3-4 shows the proposed structure for the most thermodynamically stable form of poly(2,5-furylthiophene) based on the X-ray data obtained in this model compound study.



Figure 3-4. Proposed structure of poly(2,5-furylthiophene)

The X-ray data of 1,3-di(2-furyl)thiophene, in which the oxygen is forced away from the double bond, displays the importance of the heterocycle position. Not only does this molecule exhibit three more near planar ring units within the molecule, but the rings are four times more distorted than with 2-furylthiophene.

### Coupling of Benzaldehyde, Benzaldehyde to Periodate

It was necessary to study the reproducibility of the Mukaiyama procedure for the synthesis of olefins by using coupling benzaldehyde. The experimental procedure used by Mukaiyama involved the slow addition of a suspension of zinc powder in dry THF to a mixture of  $\text{TiCl}_4$  and benzaldehyde at  $-10^\circ\text{C}$  under argon. The reaction mixture stirred for 2 hours at  $0^\circ\text{C}$ , followed by alkaline hydrolysis with 10% potassium carbonate solution, the product 1,2-diphenyl-1,2-diphenylbutene was isolated with diethyl ether extraction in a 45% yield (Figure 3-7).



Figure 3-7. Coupling of benzaldehyde to 1,2-diphenyl 1,2-ethanediol

The first modification of the Mukaiyama procedure, as was the case for the olefin formation, involved the change in the reagent addition order. The zinc was benzaldehyde was added carefully to a mixture of zinc powder and benzaldehyde in THF allowing for a quicker and cleaner addition process as well as yields above 90%. The best results, however, were obtained by utilizing the modification implemented in the formation of the model olefin compound. The  $\text{TiCl}_4$  - Zn complex is formed first by an hour reflux in THF prior to the addition of the aldehyde. This step allows the formation of a more reactive low-valent Ti species. Care was taken to cool the complex to  $0^\circ\text{C}$  before beginning the coupling process. If it was not cooled sufficiently or was allowed to warm during the reaction, there was significant formation of olefin product due to the increased reactivity of the complex. After stirring for 2 hours at  $0^\circ\text{C}$ , the reaction mixture was worked up virtually the same manner as suggested by Mukaiyama. The mixture was hydrolyzed with a 10% potassium carbonate solution followed by extraction with diethyl ether. Filtration of the mixture by products prior to extraction, however, greatly reduced the problems of

analogous formation experienced upon addition of the ester. Utilizing this modified procedure, the 1,2-diphenyl-ethanediol was obtained in a 90% isolated yield.

1-Phenyl- and 2-phenylpropanediols were again the first heterocyclic aldehydes coupled to the corresponding diols. Both products, 1,2-diphenyl-1,2-ethanediol and 1,2-diphenyl-1,3-ethanediol, were isolated in yields at high yields (90% and 90% respectively). The attempt was also made to couple 2-pyrrolidonealdehyde to the diol, but just as in the case of olefin formation, the presence of the nitrogen prevents proper isolation of the carbonyl for coupling (Figure 3-8).

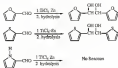
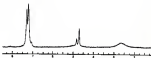
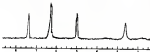


Figure 3-8. Coupling of heterocyclic aldehydes to the respective glycerol compounds

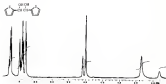
Characterization of these products, including the diphenyl testing, with proton NMR, using chromatography, revealed the formation of two different isomers (Species 3-5 through 3-7). Since the molecules possess two chiral carbons, there are exists four possible combinations of configurations: RR, SS, RS, SR, where the last two combinations are identical for these series of compounds and thus constitute the meso isomer. The first two are enantiomers and make up the *dl* (or racemic) pair (Figure 3-9).



Spectrum 3-5  $^1\text{H}$  NMR spectrum of 1,2-diphenyl-1,2-ethanediol



Spectrum 3-6  $^1\text{H}$  NMR spectrum of 1,2-diphenyl-1,2-ethanediol



Spectrum 3-7  $^1\text{H}$  NMR spectrum of 1,2-dichloroethane-1,2-diol.

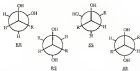


Figure 3-8 Four possible geometric isomers of a molecule possessing two chiral centers

Knowing the relative rates of the reactions of these model compounds is valuable in predicting the extent of irregularity expected in polypyranose synthesized via Molander chemistry. Which isomer is synthesized predominantly and what factors are responsible for its formation are questions which needed to be answered. Similarly, Chrus and Patai [24] coupled vanillinacetone and benzaldehyde with  $\text{TiCl}_3$  under basic conditions yielding varying amounts of the respective pyranose (Figure 3-10).



Figure 3-10 Acetophenone coupled to 1,2-dimethyl-1,2-diphenylethane-1,2-diol

The  $\alpha/\beta$  ratio for vanillinacetone was determined to be 1:7 by spectroscopic methods and is similar to the ratio observed in its photochemical [25] and electrochemical [26] reductions in dilute solutions. The  $\alpha/\beta$  ratio for benzaldehyde also reflected a predominance of the  $\beta$  isomer with a value of 1:3 but was only slightly higher than the value of 1 for cyclohexanone [27]. It is known from literature [28-30] that radicals for which steric and polar effects appear to be important, couple predominantly to  $\alpha$  or  $\beta$  diols, since interaction between like groups are maximized. The predominance of the  $\beta$  isomer for electrochemical results, however, was explained as an influence of intramolecular hydrogen bonding in the form of coupling (34,35) (Figure 3-11).

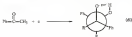


Figure 3-11 Electrochemical reduction being influenced by hydrogen bonding.

Using similar arguments, Clavier and Patai felt the large sterical hindrance of titanium for oxygen would cause bridging between the carbonyl oxygens in the case of coupling. Based on this concept, one can consider three possible orientations of the two radicals upon coupling (Figure 3-11). Of these three possibilities, two would yield *dl* isomers while the third scenario (which involves some interaction between the aromatic rings) would lead to *meso* formation.

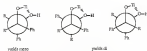


Figure 3-11. Possible orientations of coupled radical with Ti bridging

Consequently, the same stereoisomeric arguments can be applied to the present system prepared in this model compound study with the  $\text{TiCl}_3$  as complex, with the only difference being the use of a titanium surface in the formation of the bridge. Using eclipsed conformations, one can suggest two different structures for the reaction intermediates (Figure 3-12). One structure has rings which are in a "transoid" relationship, while the second structure has the rings on the same side in a "cisoid" relationship.

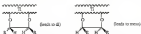


Figure 3-12. Formation of radical intermediates on a titanium surface.

The most viable intermediate is expected to be the first structure, since the extent of steric interference between the aromatic rings has been minimized. Hydrolysis of this intermediate would lead to the di isomer in a greater proportion, while hydrolysis of the less viable intermediate would yield the mono.

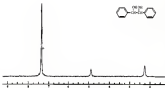
#### Experimental Evaluation of the Model Offense Again by Hansen Separation

To confirm the formation of a bridged intermediate on a titanium surface, it was necessary to experimentally verify the predominance of the di isomer in the model reaction when using the  $TiCl_4$ -Zn reduction complex. The simplest way to achieve this verification was to separate the diastereomers and characterize the individual isomers. Separation of the 1,2-diphenyl-1,2-ethanediol diastereomers was achieved by repeated recrystallizations in a diethyl-ether : petroleum ether solvent mixture. Small white crystals were obtained which possessed a melting point of 137°C (uncorrected). Comparison of melting points found in literature for the individual diastereomers [26, 33] revealed the isolated crystals to be the *trans* isomer (Table 3-4).

Table 3-4 Experimental and literature melting points for 1,2-diphenyl-1,2-ethanediol

Experimental Yield	Literature Values
(CPC)	(8): 148.2-149.5°C [20]
	(9): 142.3-146.3°C [23]
	(33): 130°C [26]
	(trans): 137°C [26]

Characterization of the crystals with proton NMR yielded a spectrum with signals at  $\delta$  1.3 (3H,  $\delta$  4.87, and  $\delta$  7.10) confirming the isolation of one diastereomer (Specimen 3-4). Comparison of these data with the original spectrum of the diastere mixture (Specimen 3-5) as well as literature values [26] suggests that *trans* isomer was formed in respect to the di isomer, supporting the concept of a bridged intermediate.



Spectrum 3-8  $^{400}\text{MHz}$   $^1\text{H}$  NMR spectrum of meso-1,2-diphenyl-1,2-ethanediol

#### Experimental Evaluation of Model-dilute Ratio Using Lanthanide Shift Reagent

Evaluation of the dilution ratio for the isotropic dilute was more difficult, since accurate values could not be found for characterization of the separated diastereomers. The dilution method was therefore analyzed by using a chemical shift reagent as differentiator between the diastereomers (Figure 3-14). The difference in chemical shifts observed for enantiomeric isomers in solutions containing chiral shift reagents arise from two mutually dependent structures: (40), the equilibrium constant for formation of the various possible diastereomeric complexes between the enantiomeric substrates and the chiral diluent dilute, and the geometries of these complexes once formed (see diagram).



Figure 3.14 Karplus shift reagent used to influence chemical shifts

The boundary of ring-current shift reagent was first demonstrated by Whittaker and Lurie (11), who observed nonequivalent species for enantiomeric amines in the presence of *rac*-[3-(*tert*-butylthio)propylthio]-*d*-camphorato] europium(II). The proton structure of the enantiomers (I and II) exhibit the expected downfield paramagnetic shift due to the interaction with the paramagnetic europium(II) ion. In a mixture of enantiomers, however, chemical shift differences ranging from 0.3 ppm for the  $C_{13}H_{27}O_2$  protons to 0.97 ppm for the para hydrogens of the benzene ring are evident.

In a communication by Fokis and coworkers (12), the use of chiral solvents and lanthanide shift reagents to distinguish enantiomers due to diastereomeric species was described. A dramatic difference between the lanthanide induced shift of the methyl protons in the *cis* vs. *trans*-2,3-butylene oxide and in *dl* enantiomer was noted (Figure 3.15)

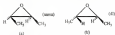


Figure 3.15 (a) *cis*-2,3-butylene oxide (b) *trans*-2,3-butylene oxide

The greater overall shifts displayed by the protons in the more common were obtained as a reflection of the fact that one of the two diastereotopically related faces of the water is more readily accessible to the transition complex than the sterically hindered face of the corresponding *dl* isomers. This phenomenon, in which steric factors control induced shifts in cyclic ether systems, was explained on the basis of either unequal populations of the two diastereomeric hemiacetal ether complexes or closer approach of the transition shift reagent to the unhindered face of the cyclic ether, both being due to steric factors.

The hemiacetal shift reagent chosen for this model compound study was tri-(1-(2,6-dichlorophenyl)hydroxymethyl)-4-carboxymethyl compound (II), since it has been shown to best affect the shifts of protons on carbon adjacent to hydroxy functional groups (H) (Figure 3-14). Since proton NMR peak assignments had already been made for 1,2-diphenyl-1,2-ethanediol, the usual hemiacetal experiment was performed on this period in order to better understand any shifts which would occur.

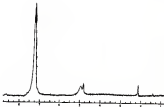


Figure 3-14. Tri-(1-(2,6-dichlorophenyl)hydroxymethyl)-4-carboxymethyl compound (II)

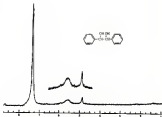
The original NMR sample consisted of approximately 10 mg. of the diol dissolved in 0.5 ml. of solvent C (deuterated chloroform with 1% TMS). After acquisition of a base spectrum (Spectrum 3-8) 2 mg. of the hemiacetal reagent was added directly to the NMR sample, shaken vigorously, and a second spectrum obtained (Spectrum 3-9). The most remarkable change in the spectrum involved the  $\text{C}(\text{OH})$  proton peak for the more common *rac*: 2.4  $\delta$ , which shifted 0.15 ppm downfield and broadened. The corresponding *dl* peak also

shifted about 2-10 ppm downfield but maintained its original line width. In addition, the two singlets in the aromatic region remained relatively stable but showed signs of coalescing, while the broad signal for the hydroxyl protons narrowed.

After the addition of another 4 mg. of the europium-complex, further changes in the spectrum were observed (Spectrum 3-10). The signal for the methoxy protons peak now showed a significant shift of 5-6 ppm further downfield with an increase in broadening. The corresponding peak for the  $\alpha$  protons, however, shifted a modest 0-10 ppm further and maintained its position in original line width. Interestingly, the two aromatic signals, which originally appeared at  $\delta$  7.19 and  $\delta$  7.26, had now coalesced completely into one signal at  $\delta$  7.3.



Spectrum 3-10:  $^1\text{H}$  NMR spectrum of 1,2-diphenyl-1,2-ethanediol with 2 mg shift reagent.



Spectrum 3.10.  $^1\text{H}$  NMR spectrum of 1,2-diphenyl-1,2-ethanediol with long shift reagent.

Since it was now known that the lanthanide complex would affect the shifts of the diastereomers to varying degrees, the experiment was repeated with 1,2-dibenzyl-1,2-ethanediol. The two spectrum displayed the expected dual signal at  $\delta$  3.0 and  $\delta$  3.1 for the  $\text{CH}_2\text{CH}$  protons of each diastereomer (Spectrum 3.11a). The quartet in the aromatic was much peak represented the meta isomer and which peak represented the all isomer. Upon addition of 4 mg of the europium reagent, the larger of the two peaks at  $\delta$  3.0 shifted 0.4 ppm downfield. The smaller peak, however, shifted 1.05 ppm, substantially broadened, and showed signs of forming a doublet (Spectrum 3.11b).

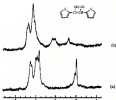


Figure 3-11. (a) Base  $^1\text{H}$  NMR spectrum of 1,2-dithienyl-1,2-ethanediol.  
(b)  $^1\text{H}$  NMR spectrum of 1,2-dithienyl-1,2-ethanediol with 4 mg shift reagent.

Comparison of the thienyl-diol oxides with those obtained earlier with the phenyl-diol, further verified that the *dl* isomer was formed predominantly over the *meso* isomer, while at the same time supported the concept of a bridged intermediate proposed in the literature [12, 16].

The results of this model compound study with the benzenediol shift reagent are similar to those obtained by Ceresa and coworkers [44], who synthesized a diastereoisomeric mixture of bis(phenylsulfonyl)oxetane by oxidation of bis(phenylthio)oxetane with hydrogen peroxide (Figure 3-17).



Figure 3-17 Oxidation of bis(phenylthio)propane to bis(phenylsulfinyl)propane

The monomer monomer has equivalent  $\text{CH}_2$  protons while those in the monomer should be non-equivalent. The spectra of each monomer, however, showed  $\text{CH}_2$  regions at  $\delta$  4.17 for the lower melting point and  $\delta$  4.84 for the higher melting monomer. Thus, the non-equivalent  $\text{CH}_2$  protons in the more complex must have the same chemical shift. In the presence of a chiral shift reagent, though, these two protons of the more complex would now be expected to show different chemical shifts. Grosse and coworkers found that in the presence of methylcyclopentadienyl tungsten (III), the protons of the lower melting point monomer were split into an AB quartet ( $\delta$  5.90 and  $\delta$  6.12) and thus assigned to the more complex. The  $\text{CH}_2$  protons in the higher melting monomer remained a singlet, although shifted to  $\delta$  5.64, and was assigned to the di monomer. They proposed through the use of models that coordination of the complex takes place at the oxygen atoms.

Applying this information from Grosse as well as that discussed above by Perle et al.<sup>142</sup>, it became possible to understand the changes in shift and multiplicity observed with the phenols in the model compound study. Since the hydroxide reagent is expected to complex to both hydroxy groups, it would approach in such a way to minimize steric interaction with the larger substituents. In the case of the more complex, the oxygen would approach the side away from the acetate (or bromoacetate) rings. With the di pair, however, the tungsten-containing equal interaction with the rings regardless of the direction of approach. Favoring formation of a symmetrical complex (Figure 3-14).



Figure 3.18. TiO<sub>2</sub> surface complexing with trans and cis isomers

Since the hydroxyl groups are more accessible in the *cis* isomer, the reaction with the *cis* isomer is more extensive, explaining the greater shift for the  $\text{C}_2\text{H}_4\text{O}_2$  protons. With these models it also becomes possible to see the asymmetric nature of the *cis* complex, which places the two  $\text{C}_2\text{H}_4\text{O}_2$  protons in different magnetic environments, causing the observed splitting. In the case of the *all* isomer, the symmetry of the molecule is maintained. Thus, the  $\text{C}_2\text{H}_4\text{O}_2$  protons remain in the same environment (resulting in the slightly shifted singlet).

#### Investigation into the Mechanism of Hydrolysis

One point which has not been addressed in the literature is the mechanism involved in the hydrolysis of the intermediate after formation of the bridged complex. Based on the work already presented on the evolution of the diastereomer mixtures, one might assume that hydrolysis involves the initial attack of the lone valent titanium bridge followed by the subsequent cleavage of the Ti-O bond with protonation of the *cis* oxygen to form the hydroxyl functional groups (Figure 3.19). The assumption of this mechanistic route is that the oxygen bound to the *cis* that are the *cis* oxygen bound to the original doublet prior to coupling.

Titanium has a strong affinity for oxygen, however, resulting in a bond which is roughly two and a half times stronger than that for  $\text{C-OH}$ , (4). Consideration of this fact allows the proposal of a second possible mechanistic route, where a  $\text{H}_2\text{O}$  molecule of the water in the matrix attacks, resulting in cleavage of the original  $\text{C-O}$  bond and an inversion of configuration at that site (Figure 3-20). In this scenario, the oxygen bound to the final

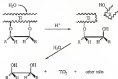


Figure 3-19. Mechanism involving axial attack at the titanium surface upon hydrolysis.

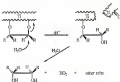


Figure 3-20. Mechanism involving an axial substitution attack at the distal carbon.

product are the results of hydrolysis, while the original acylaryl moieties are now part of the ketone-imide by-products.

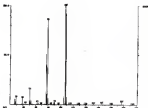
In an attempt to differentiate between these two cases, benzaldehyde coupling reaction was repeated using water labeled with 99%  $^{18}\text{O}$ -during the final hydrolysis step. The reaction was sealed down such that only 0.5 ml of water was required for hydrolysis. Mass spectroscopy of the diol was performed, and compared with a mass spectrum of the same diol obtained with normal hydrolysis. If the hydrolysis step were to proceed through the substitution route, then the labeled  $^{18}\text{O}$  would be incorporated into the final product as hydroxy functional groups.

Results of the mass spectra comparison conclusively show no evidence of  $^{18}\text{O}$  incorporation (Spectra 3-18 and 3-19), and thus, the oxygen present in the diol are the same oxygen-atoms in the original aldehyde. Therefore, the chemistry in Figure 3-18 is correct.

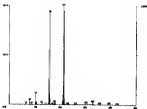
This model compound study was instrumental in obtaining a range of information necessary for the synthesis of McMurry chemistry in ring polymerization. The study demonstrated that the near quantitative-coupling of aromatic carboxylic-acids using Mukaiyama's system can be extended to heterocyclics for both olefin and pinacol formation if modifications are made to Mukaiyama's procedure. Pyrrole and pyridine analogs are analogous to the pyrimidines, most nitrogen complexes to the imidative system preventing coupling. In every case during this study, the main barrier was formed almost exclusively. In addition, X-ray structural analysis of the olefins yielded unequivocal data concerning the varying extent of "chain-end" over build in changing from aromatic to heterocyclic systems. The pinacol model compound study characterized the isomers formed by the Mukaiyama system, verifying McMurry's prediction of a cyclic pinacolide intermediate.

Extension of these model compound studies to the formation of polymericols, allowed the following prediction to be made. Regardless of the monomer coupled, the resulting polymer will not have a high extent of stereoregularity but will possess a medium

distribution of repeat units of varying configurations, with the all configurations occurring predominantly. Each polymer tend to be amorphous, since the close packing necessary for crystallization is not possible.



Spectrum 3.11: Mass spectrum of 1,2-epibromyl-1,2-ethanediol after normal hydrolysis.



Spectrum 3.18 Mass spectrum of 1,2-dithienyl-1,2-ethenediol after hydrolysis with  $^{18}\text{O}$ -labelled water

## CHAPTER 4 AN INVESTIGATION OF POLYMERIZATION VIA REDUCTIVE COUPLING OF CARBONYLS

Using information obtained from the model compound study, an investigation of the polymerization of cyclohexyl with low-valent titanium was undertaken. Since Malacyszyn and co-workers [8] demonstrated that only aromatic aldehydes and ketones could be coupled in near quantitative yields, all monomers polymerized in this study possessed aromatic moieties. The model compound study, however, showed that the ability to obtain high yields extended to heteroaromatics, thereby allowing polymerization of a heterocyclic dialdehyde. The purpose of this study was to evaluate the viability of ring polymerization with the Malacyszyn system to produce both polyarylenes and polyimides, with the isolated polymers characterized for purity, structure, and molecular weight.

### Polymerization of Polyarylene Formamides

Terephthalaldehyde was the first monomer polymerized, with care taken to obtain high purity monomers by successive recrystallization and sublimation. A successful polymerization under sulfur conditions would yield poly[1,4-phenylenearylene] (Figure 4-1).



Figure 4-1. Polymerization of terephthalaldehyde to poly[1,4-phenylenearylene].

In the first synthetic stage of the polycondensation, the procedure was essentially the same as for the synthesis of the model olefin compounds. The induction complex was formed *in situ* by refluxing  $\text{TiCl}_4$  with Zn powder in THF, and the monomer, amphiphilolefin, was added to the complex and refluxed for 18 hours. The duration of reflux for this stage of the reaction was increased five times over the model compounds to ensure complete coupling of all available carbonyls. As this point work-up procedures were modified from steps used in the synthesis of the model olefins, due to the variability of the expected polymer. An aqueous solution of 10% potassium manganate was added, which not only quenched the reaction but also precipitated titanium by-products. These solids were filtered, and the filtrate was washed with several fractions of diethyl-ether. Evaporation of the ether, however, yielded only a yellow-oily film. Since no amphiphilolefin was isolated, all monomer was believed to be consumed.

The solid film (cake) was returned to a flask containing THF and refluxed for several hours. During this period the solvent slowly turned yellow (indicating possible formation of poly(phenylacetylene)) [47]. After filtration and solvent removal, however, a yellow oil was again the only substance isolated.

Extraction was repeated using DMSO, and the solution again became yellow; however, the color was darker and fluorescent. After filtration, the solution was slowly dropped into several hundred milliliters of water resulting in the slow precipitation of a yellow solid.

Elemental analysis revealed the presence of a high amount of impurities with the experimental carbon value being slightly more than half of its theoretical value (Table 4-1). Such a discrepancy could only be caused by a large amount of titanium salt incorporated into the polymer.

Infrared spectroscopy of the product supported this explanation, with a broad absorption from 1100 to 600  $\text{cm}^{-1}$  which is representative of a Ti-O absorption [24]. This

same signal is also visible in the IR spectrum of the orange filter cake (Spectra 4-1 and 4-7)

Isoprene contamination can partly be explained by an ESR isomerization performed by Durr and coworkers on a  $\text{TiCl}_3$ -LiAlH<sub>4</sub>-mucous mixture [14]. They found that immediately after deoxygenation to the diene, a Ti(ED) species existed it bonded to the product diene and the mixture is worked up. Therefore, it is feasible that a bonding allows isoprene to become incorporated into the polymer matrix, making it difficult to separate from the product, even after hydrolysis work up.

In an attempt to purify the product, the polymer was refluxed in DMF and once again precipitated in several hundred milliliters of water. Filtration of the resulting solid left a yellow film on the filter paper which becomes transparent and brick-red on drying. Elemental analysis of the film showed a dramatic improvement in the purity of the product, even though contamination was still evident (Table 4-3). Likewise, the corresponding IR spectrum showed little evidence of isoprene incorporation into the polymer (Spectra 4-3).

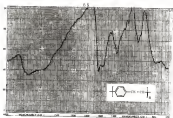
Table 4-1. Elemental analysis of crude poly(phenylacetylene)

Element	Theory	Experimental
C	94.12%	93.32%
H	5.88%	5.94%

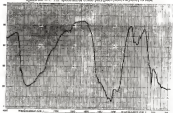
Table 4-2. Elemental analysis of poly(phenylacetylene) after reprecipitation from DMF.

Element	Theory	Experimental
C	94.12%	96.62%
H	5.88%	5.79%

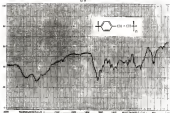
NMR analysis of the yellow polymer was very difficult due to its low solubility. Using  $\text{DMSO}-d_6$  and allowing a long acquisition time, a proton spectrum was obtained



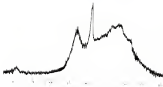
Spectrum 4-1. IR spectrum of atactic poly(styrene-vinylene) in KBr



Spectrum 4-2. IR spectrum of McNary Chemistry by product in KBr



Spectrum 4-3 IR spectrum of poly(phenylacetylene) precipitated from DMF



Spectrum 4-4  $^1\text{H}$  NMR spectrum of poly(phenylacetylene)

(Spectrum 4-8) showing a broad signal from  $\delta$  6.2 to  $\delta$  8.7 for the aromatic protons and a narrower signal at  $\delta$  7.9 for the vinyl protons. In addition, a small peak at  $\delta$  9.9 was visible representing unreacted aldehyde-end groups. This fact would suggest that the reaction was not complete, since aldehydes were still present. However, extending the reaction time had little or no effect on the outcome of the polymerization.

The next monomer polymerized was 1,2-diphenylcyclohexene. Although the resulting polymer does not have a conjugated backbone, it is a precursor to head-to-head polystyrene (Figure 4-5).

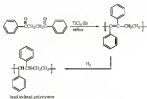


Figure 4-5. Attempted polymerization of 1,2-diphenylcyclohexene.

The procedure followed was the same as that used for vinylcyclohexene. Characterization of the compound, however, revealed that instead of the expected unimolecular polymerization of the monomer, unimolecular-coupling occurred leading to the cyclized product, 1,2-diphenyl-cyclobutene (Figure 4-3). Although cyclization was

unsaturated bond on the ring atom is cyclization, it is not without precedent. Eisenberg *et al.* [12] demonstrated the same cyclization of 1,2-diphenylglyoxal in a  $\text{TiCl}_3/\text{LiAlH}_4$  system.



Figure 4-3 Cyclization of 1,2-diphenylglyoxal to 1,2-diphenylcyclobutene

To avoid the cyclization, *trans*-1,2-diphenylglyoxal was used as the monomer. It was expected that having a double bond present with a *trans*-configuration would prevent intramolecular coupling of the carbonyls. The resulting polymer,  $\text{poly}[\text{trans-1,2-diphenylglyoxal}]$ , now has a fully conjugated backbone (Figure 4-4).

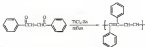
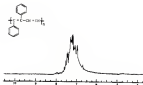


Figure 4-4 Polymerization of *trans*-1,2-diphenylglyoxal to  $\text{poly}[\text{trans-1,2-diphenylglyoxal}]$

Standard procedure was followed except for the work up which was done under inert atmosphere to reduce possible oxidation of the product. Washing the filter with ethyl ether yielded a yellow oil as before. The remaining blue filter cake was placed in a Soxhlet extractor, and refluxed in THF in the extractor for two days, yielding a yellow oil which was more viscous than the oil obtained from the ether, signifying an increase in



Spectrum 4-5  $^1\text{H}$  NMR spectrum of poly[1,3-diphenylthiazane]

molecular weight of the polymer. Proton NMR analysis of both oils gave nearly identical spectra with a broad multiplet from 2.4 to 2.7  $\delta$ , supporting a repeat unit possessing two phenyl rings and two vinyl groups (Spectrum 4-5).

In an attempt to obtain higher molecular weight polymer, the Soxhlet extraction was done with DMSO as the refluxing solvent. During extraction the solvent slowly changed color from clear colorless to dark cloudy yellow. After 36 hours DMSO was removed by rotary evaporation leaving behind a brown powder, and analysis of the solid showed it to be mainly undetectable inorganic oils generated during the coupling reaction.

The final monomer reacted with the TSCs, its complex in an attempt to make a high molecular weight polythiophene was 2,5-diacetoxaldehyde form. A second(1) polymerization would yield poly[2,5-thiophenethiophene] (Figure 4-6).



Figure 4-5 Polymerization of 2,5-diacetylsalicylic acid to poly(2,5-thienophenylene)

Using the same procedure as before, nothing more than small amounts of a material could be isolated. Visual inspection of the by-product revealed the presence of small orange colored flakes which were believed to be polymer, but every attempt to separate them from the unreacted acid failed to be successful.

Polymers of the type obtained from other ring-substituted polycondensations revealed the problems involved in the processing of polymers with rigid-conjugated backbones. Based on the color of the material during work-up (brown yellow for poly(phenylacetylene) [10]), coupling of the carboxylic appears to have taken place. The polymer, however, apparently reaches a limiting molecular weight after which it becomes insoluble and precipitates. In most cases only a low molecular weight oil was isolated. When higher molecular weight fractions were isolated, they were contaminated with unreacted acid.

### Investigation of Polymer Formation

The investigation into possible locations of polymers with McMurry chemistry was first extended to the case of polyketones where the presence of hydroxy functional groups would make the polymers more soluble and easier to isolate. Two monomers were chosen, 4-oxocyclohexanecarbaldehyde and 2,5-diacetylsalicylic acid, which if suitably polymerized, would yield poly(1,4-cyclohexene-1,1-dimethylene) and poly(2,5-thienyl-1,2-dithienylene) respectively (Figure 4-6).

As in the case for polyphenylene formation, the  $\text{TiCl}_4/\text{Zn}$  complex was formed in advance in THF and cooled to  $-78^\circ\text{C}$  before the addition of monomer. This temperature was carefully maintained while the mixture stirred for 2 to 10 hours, after which it was hydrolyzed with a 10% potassium-ethoxide solution and the resulting orange solids

filter). The molecular weight of the product depended greatly on the length of reaction time. When the reaction mixture was allowed to react for only two hours, the resulting polymer was still an oil-soluble and therefore was removed from the filter. As the reaction

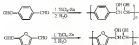
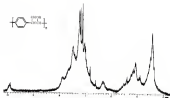


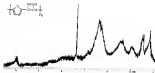
Figure 4-6. Polymerization of dialdehydes to their respective poly(p-phenylene)s

time increased, however, the amount of polymer bound to the filter was reduced, suggesting a higher-molecular-weight product had been formed. It soon became necessary to refine the inorganic filter cake in THF to isolate product, much like the method necessary in the attempted isolation of poly-oxepanes. Polymers were purified by reprecipitation in hexane. Elemental analysis of the two polymers gave acceptable correlations to the theoretical values for each.

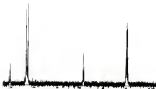
Comparison of the proton NMR spectra of the polymers with the spectra of the analogous model compound supported the formation of the expected diol repeat units. The hydroxy signals, however, had shifted downfield in both cases. As in the case of the model compounds, representative peaks for the *meta*- and *ortho*-protons within the polymer chains are recognizable, confirming the presence of a stereochemically random polymer. A major element in the polymer spectra is the presence of an aldehyde peak at 2.7 ppm for poly(p-phenylene-2,5-dihydroxybenzylidene) and 2.18 ppm for poly(p-phenylene-2,6-dihydroxybenzylidene), signifying that the reaction had not gone to completion (spectra 4-6 and 4-7).



Spectrum 4-6: <sup>1</sup>H NMR spectrum of poly(phosphazene-ethyleneoxy)



Spectrum 4-7: <sup>1</sup>H NMR spectrum of poly(fluorene-ethyleneoxy)



Spectrum 4-3.  $^{13}\text{C}$  NMR spectrum of poly(p-terephthale-n-ethylmaleate).

Lengthening the reaction time past 30 hours had little or no effect on the extent of reaction, but instead increased the amount of olefin formation. Olefin signals were visible in the proton spectra for both poly(p-terephthale-n-ethylmaleate) and poly(p-arylene-n-ethylmaleate) at 2.7-2 and 2.7-4, respectively, as well as in the  $^{13}\text{C}$  spectrum of PPED at 2.141 (Spectrum 4-3).

### Molecular Weight Determinations

#### End-Group Analysis

Initial molecular weight assessments of poly(p-terephthale-n-ethylmaleate), poly(p-arylene-n-ethylmaleate), and poly(p-terephthale-n-ethylmaleate) were made by an end-group analysis using the unsaturation data obtained from the proton NMR spectrum for each polymer. The olefinic peaks in each case are representative of the unreacted end-groups for the polymer, and by a comparison of their relative integration values with that of the

molecule, a number-average degree of polymerization  $\overline{X}_n$  was calculated, leading to number-average molecular weight  $\overline{M}_n$  values of 1050, 2050 and 3140 for the three polymers, respectively (Table 4-3). To use this method, however, the assumption had to be made that all end-groups were nitrileides. If that were not the case, then the calculated molecular weights would be unacceptably high.

Table 4-3 Degree of polymerization and molecular weights for polymers synthesized.

Polymer	polymer/nitrileide	$\overline{X}_n$	$\overline{M}_n$
poly(phenyleneacetylene)	96.47 / 9.33	9	1050
poly(phenylene-ethylene)	98.79 / 1.21	20	2050
poly(harylene-ethylene)	94.05 / 0.95	43	3140

### Vapor Pressure Osmometry

Due to the uncertainty involved in the use of end-group-analysis for a molecular weight evaluation of these polymers, vapor pressure osmometry (VPO) was used to obtain a comparative value. Due to the low solubility of the polymers, dimethyl sulfoxide was chosen as the solvent and the temperature of the apparatus set at 103°C. Using benzol as a standard, a calibration constant of 448 was obtained, which was then used to calculate the molecular weight of the polymers. A  $\overline{M}_n$  value of approximately 3050 for poly(phenylene-ethylene) was determined, which is slightly less than the value of 3140 obtained using end-group analysis. The molecular weights of poly(phenyleneacetylene) and poly(harylene-ethylene) could not be obtained using this method, since the corresponding solutions were apparently too dilute to create an effective (or reproducible) change in the relative vapor pressure of 0.0025.

### Discussion of Polymerization Mechanisms

The two molecular weight values obtained for poly(p-benzylbenz-o-biphenol) in this study correspond well enough to verify the assumption that the majority of polymer end-groups are aldehydes. If the polymer chains still possessed carbonyl functionalities, why did they not continue to couple and form higher molecular weight polymer? One possibility might be insufficient reaction times, yet it has already been shown that lengthening the reaction times had little or no effect on the molecular weight of the polymers. Answering this question, therefore, requires an understanding of the additional mechanistic features involved in the formation of polymers using telechelic chemistry.

### Additional Mechanistic Steps Involved in Telechelic Polymer Formation

Although the monomers possess two carbonyl per molecule, only one of them is reduced within a given time frame prior to coupling. Therefore, the rate of coupling is faster than the rate of reduction due to the reactivity of the radical anions. The initial step therefore involves formation of a dimer complex possessing an unreacted carbonyl at each end (Figure 4-5).

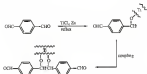


Figure 4-5 Formation of dimer complex during initial steps of polymerization.

At this point, two processes can occur (Figure 4-4). One process (option 1) involves further reduction of another carbonyl to a radical anion resulting in rapid coupling with nitroxide or another donor. The second process (option 2) involves the subsequent decarboxylation of the intermediate resulting cyclic formation. There is some discrepancy in the literature, however, concerning which of these two processes occurs more rapidly. McMurry [11] reported that the rate-determining step in the coupling is cyclic must involve loss of oxygen from the pinacolborane intermediate, but that decarboxylation should be easier in aromatic cases than in aliphatic cases since the C-C bond involved is benzylic. In the mechanistic study performed by Dams and coworkers [12], however, the rate-determining step is said to be the decarboxylation and not the cleavage of the oxygen.

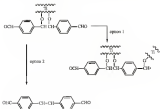


Figure 4-4 Second stage of polyaromatic synthesis involving one of two route options

Considering the information as well as the molecular weight data obtained for poly(phosphazenes) itself, the rate of decarboxylation during the polymerization must be faster than the rate of radical reduction. The result of this process is slow formation of the polyurethane while maintaining carboxyl end-groups. When an aldehyde is reduced, coupling then occurs extending the chain, followed by decarboxylation of the urethane. The growth of the polymer chain continues as this sequence until a reaches the limiting molecular weight leading to precipitation. Once the polymer has precipitated, polyurethane moieties and the carboxylic acid no longer is susceptible to reduction, thus, the end groups remain intact.

### Mechanistic Steps Involved in Polyurethane Formation

The initial steps in the mechanism for polyurethane formation are the same as described for the polyurethane case. A carboxyl on the monomer molecule is reduced to a radical anion and couples with another radical anion along a reaction surface forming the intermediate chain. Since the temperature is maintained at 0°C, decarboxylation does not occur and is therefore not a factor in the polymerization mechanism. Consequently, the polymer chain continues to elongate while remaining complexed to the monomer (Figure 4-14).

Since the developing backbone is saturated and therefore more flexible than a polyurethane, the polyurethane is more soluble and remains in solution longer, allowing a more complete reduction of the aldehyde portion. This result explains the increase in amounts of success from 0.48 for poly(phosphazenes) to 0.83 for poly(phosphazene ethylenediol) and 0.96 for poly(phosphazene ethylenediol). Even with the increased flexibility of the polymer backbone, however, there still exists a limiting chain length after which poor reduction of the remaining carboxyl end groups occurs. Once this point has been reached, the length of reaction time is no longer a factor. In fact, longer reaction times usually resulted in a higher amount of reduced-chain formation.

The final step of the reaction is the hydrolysis of the intermediate polymer to the corresponding polypyrrocol. Even though this step proceeds as a reaction similar to that for model compounds, longer reaction times were allowed to ensure complete hydrolysis.

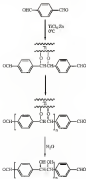


Figure 4-9 Polymerization mechanism leading to formation of a polypyrrocol.

## CHAPTER 3 AN INVITATION INTO METHODS FOR INCREASING POLY(ETHYLENE) SOLUBILITY

It was demonstrated in the synthesis of polyacrylates using McMurry chemistry that polymers possessing rigid backbones have low solubility in organic solvents, with processing, characterization, and even simple purification being difficult tasks to perform. This phase of the research, therefore, dealt with an investigation into possible methods for increasing polyacrylate solubility. A great amount of research has been dedicated to overcoming the problems of low solubility with varying results [41-50]. Presently, that work can be categorized into two major areas of interest: the presence of solubilizing side groups in the polymer chain and the formation of soluble polymer precursors.

### Free and Frozen Methods for Increasing Polyacrylate Solubility

#### The Presence of Solubilizing Side Groups in the Polymer Chain

In 1986 Sam et al. [44] prepared miscible polyacrylates, which are soluble in ordinary organic solvents at ambient temperatures, by electrochemical polymerization of diacrylate monomers having a long alkyl substituent. The polyalkylacrylates examined were poly(1-hexylacrylate) (PHA), poly(1-octylacrylate) (POA), poly(1-dodecylacrylate) (PDAA), poly(1-tetradecylacrylate) (PTAA), and poly(1-octadecylacrylate) (PTTA), with the conductivities of these crosslinked films being 95, 76, 67, 13, and 11 S-cm<sup>-1</sup>, respectively (Figure 3-1). The degree of polymerization decreased as the length of the alkyl substituent grew. Paul et al. [46] extended this concept by placing a sulfonic acid group on the alkyl side chain which allows for water solubility, however, only polymers with degrees of polymerizations of 3 and 4 are reported (Figure 3-2).

There are disadvantages, however, in obtaining solubility using the solubilizing side chain. Since many of these side groups are bulky, they can have an adverse effect on the morphology of the conductive polymer. Steric interactions can lead to twisting, twisting causing it to overlap as well as preventing the close packing of chains necessary for conductive interactions. This effect is clearly demonstrated in the work of Sano et al.[46], where the conductivity rapidly drops as the length of the alkyl side-chain increases.

### The Formation of Soluble Polymer Precursors

These precursors were to obtain highly conjugated polymers was first investigated in PBT by Murai et al. who considered dehydrohalogenation of polyarylethanes with aim to form polyacetylenes [30]. The precursors were obtained by radical polymerization of vinylhalides with peroxides to yield the high molecular weight polymer. They found, however, that under the extreme conditions used for the oligomerization, crosslinking occurred along with formation of cyclopropane units (Figure 3-3).

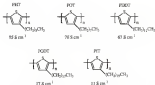


Figure 3-3. Polyarylethanes with alkyl side groups to improve solubility

Pace and coworkers (31-33) have done the most extensive study of precursor zones for polyacrylonitrile in fact. Their approach involves synthesizing the precursor polymer by a radical ring-opening polymerization of monomers like 1,3 bis(haloacetoxy) (e.g., poly(4,2,2 Cl<sup>3</sup>)) (see 3,7,9-riotes).



Figure 3-2. Polyacrylonitrile with a sodium sulfonate side group for water solubility

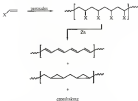


Figure 3-3. Precursor zone to polyacrylonitrile prepared by Marvel et al.

The precursor polymers formed are soluble materials which can be purified by simple reprecipitation, then cast into films or fibers from solution. 1,3-bis (trifluoromethyl)-benzene is then thermally eliminated from the precursor polymer to form (a) polynorbornene which can be cast as films (polynorbornene at higher temperature (Figure 3-4).

Wick et al. (26) used a similar approach in the formation of polythienylnorbornene and polythienylisobornylene by reacting with precursor polymers which possessed a solubilizing trifluoromethyl chloride side group in each repeat unit. Once the precursor is processed into films, the trifluoromethyl chloride is thermally eliminated producing the conjugated system (Figure 3-5).

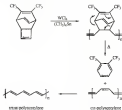


Figure 3-4 Precursor route by Fieser et al. using substituted ring-opening polymerization

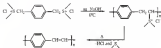


Figure 3.3. Precursor route to poly(p-phenylenevinylene) used by Wadoff et al.

Although the precursor method is generally accepted as being a successful procedure, it does possess disadvantages. Very often the chemistry involved in the synthesis of the precursor is cumbersome and difficult to control. In addition the elimination process is often incomplete, resulting in short conjugation lengths within the polymer backbone.

### A New Approach to Soluble Polycarbonates

The inability to isolate the polycarbonate formed via McMurry chemistry forced a consideration of possible modifications to improve solubility, other than the two examples already discussed. A new approach was explored in the course of this work, which combines advantages from both stabilizing side groups and generative methods. Like the work of Imai and coworkers [42], who used alkyl side groups to improve solubility, this new approach involves the placement of a strong bulky group on the monomer, but an add-on acts as a chemical "trigger" which allows the side group once the polymer has been formed and processed (Figure 3.4).

Fineman and Wilcox [27] described an efficient synthesis route to pure high molecular weight poly(p-phenylenevinylene) by first synthesizing a precursor polymer possessing a *tert*-butoxycarbonyl (*t*-BOC) protecting group (Figure 3.5). The purpose of the *t*-BOC is that

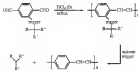


Figure 5-6. Polymerization with a bulky side group released by a chemical trigger

can it to protect the hydroxy group during radical oxidation (or cationic oxidation in liquid  $\text{SO}_2$ ) of *p*-hydroxystyrene. Once the precursor polymer has been formed, the *t*-BOC group is removed by thermal elimination of carbon dioxide and 3-methylpropene at  $200^\circ\text{C}$ . Analysis of the polymer after heating to  $200^\circ\text{C}$  shows that it consists of pure poly(*p*-hydroxystyrene) produced by the thermolysis of the *t*-BOC protecting group with evolution of one molecule of carbon dioxide and one molecule of 3-methylpropene per *t*-BOC group.

Although the original purpose of the *t*-BOC group in this work was to protect the hydroxy functionality, its name tells should render such polymer chains soluble, as was experienced by Imai et al.<sup>[48]</sup> with alkyl side groups. The advantage over the method of Imai and Wall, however, is that the side groups can be completely removed, once the polymer has been processed to the desired form.

The new approach, therefore, would be to prepare an aromatic dihalide possessing the *t*-BOC group, which could then be polymerized by the McMurry reaction (Figure 5-8). The resulting polymer would be soluble and processible allowing formation of films. Once processing was complete, the *t*-BOC group could be quantitatively removed by heating the polymer in solid state to  $150^\circ\text{C}$ .

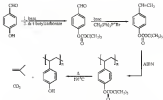


Figure 3-7 Protection of poly(cyanoacrylate) using t-BOC as a protecting group

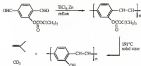


Figure 3-8 Use of t-BOC as a solubilizing side group in the synthesis of polyacetaldehyde

A model compound study was done to verify if coupling of an aldehyde compound possessing a t-BOC group is feasible utilizing McMurry chemistry. The model aldehyde, *p*-tert-butylbenzylaldehyde, was synthesized starting at *p*-tert-butylbenzoic acid with *p*-tolylmagnesium chloride ( $\text{Mg}$ ), and the compound was exposed to the  $\text{TiCl}_4/\text{Zn}$

complex in THF under reflux conditions is an attempt to synthesize 4,4'-di(hydroxy-carbonyloxy)stilbene. If coupling indeed had occurred, then heating of the compound would remove the t-BOC groups yielding 4,4'-dihydroxystilbene. Analysis of the initial product, however, revealed that 4,4'-dihydroxystilbene had been formed immediately (Spectra 5-1 and 5-2). While coupling of the aldehyde had been successful, the t-BOC protecting groups were removed prematurely in the process (Figure 5-5).

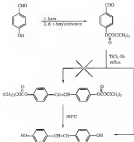
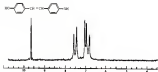
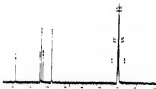


Figure 5-5. Attempted coupling of *p*-hydroxybenzaldehyde with the t-BOC side group



Spectrum S-1.  $^1\text{H}$  NMR spectrum of 4,4'-dihydroxybiphenyl.



Spectrum S-2.  $^{13}\text{C}$  NMR spectrum of 4,4'-dihydroxybiphenyl.

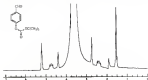
Initial speculation was that the temperature of reflux, though well below the 181 °C used for the removal of the *n*-BzOC groups, contributed to their premature elimination. An experiment was therefore designed to allow exposure of the model aldehyde to the redoxive complex in the absence of reflux conditions. In addition, aliquot samples of the reaction mixture were taken at varying times for proton NMR analysis. The solvent used in the reaction was changed from tetrahydrofuran to *p*-dioxane to assure that the NMR signal for the anthryl group would be visible.

The actual aliquot was removed at the beginning of the reaction with only the aldehyde and 2*n*-pentyl *n*-dioxane. NMR signals for the (broad) protons, the aromatic protons, and the aldehyde proton were clearly visible at  $\delta$  1.40,  $\delta$  7.70, and  $\delta$  10.12 respectively. The reaction mixture was cooled to -18 °C, followed by careful addition of the  $\text{TiCl}_4$ . An aliquot of the green-yellow solution was removed for proton NMR analysis. The aldehyde and aromatic signals were barely visible, while two signals were excited in the  $\alpha$ -(broad) region at  $\delta$  1.58 and  $\delta$  1.60 with a signal ratio of about 2 to 1. The reaction continued in air under argon at -18 °C, while slowly darkening in color. After 30 minutes another aliquot of the dark blue solution was taken, however spectral analysis revealed no visible signals other than the broad dioxane peak at  $\delta$  3.55 (Spectra 3-3 and 3-4).

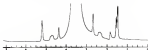
Interpretation of these results suggests that even at low temperatures the *n*-BzOC group cannot survive exposure to the redoxive complex. The second NMR spectrum shows a significant decrease in the intensity of anthryl signal at  $\delta$  1.60 while a second  $\alpha$ -(broad) signal appears at  $\delta$  1.50. This second signal represents the *n*-BzOC group in solution, having been removed from the ring. Work up of the reaction afforded mostly *p*-hydroxy benzaldehyde. The reaction conditions were modified to allow substantial coupling, but were strong enough to remove the *n*-BzOC group.

This model compound work demonstrated that the concept of using *n*-BzOC groups in the polymerization of conductive polymers with McElveny chemistry is not a feasible process. However, the use of such *n* group with other polymerizations has not been

arrangement. Some conductive polymers can be synthesized by a variety of different methods: a reaction system in which the  $\pi$ -BDC group can convert itself into



Spectrum 3-3: <sup>1</sup>H NMR spectrum of *p*-1-BDCbenzothiole in dioxane with Zn.



Spectrum 3-4: <sup>1</sup>H NMR spectrum of *p*-1-BDCbenzothiole in dioxane with TiCl<sub>4</sub>-Zn.

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## BIOGRAPHICAL SKETCH

Anthony Wayne Cooke was born June 8, 1941 in Charlotte, North Carolina. In 1959 he began his undergraduate work at the University of North Carolina at Asheville, where he studied both chemistry and German. Wayne received his BS in chemistry in 1963, graduating cum laude with distinction in chemistry. In addition he was awarded a Fulbright Scholarship to conduct research for a year at Phillips University in Marburg, West Germany, under the direction of Dr. Jürgen-Pekler.

Upon returning to the United States in 1964, Wayne commenced his graduate studies at the University of Florida, where he studied with Prof. Kenneth B. Waggoner, while receiving fellowships from both IBM and the Francis I. Newton Foundation. Unfortunately during this time, Wayne's father, Lewis, made the crucial mistake of treating his son the sport of golf. Wayne eventually forgives his father and drops his addiction to the game, received his PhD in organic chemistry in 1967. Shortly thereafter, Wayne left graduate life and returned to North Carolina with his wife, Laura, where he began a career in industry with the Riedel Chemical Corporation.

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

  
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Associate Professor of Chemistry

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Professor of Chemistry

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Professor of Chemistry

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This dissertation was submitted to the Graduate Faculty of the Department of Chemistry in the College of Liberal Arts and Sciences and to the Graduate School and was accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

May 1993

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Dean, Graduate School